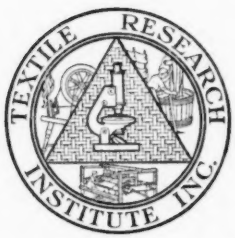
TEXTILE RESEARCH JOURNAL

VOLUME XIX March, 1949 *NUMBER 3*



PUBLICATION OF

TEXTILE RESEARCH INSTITUTE, INC.

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TEXTILE RESEARCH JOURNAL

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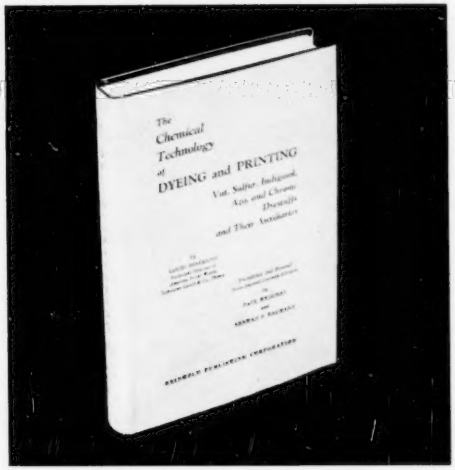
By Louis Diserens

Technical Director of Alsatian Print Works, Scheurer-Lauth & Co., Thann. Translated and Revised from Second German Edition by Paul Wengraf and Herman P. Baumann



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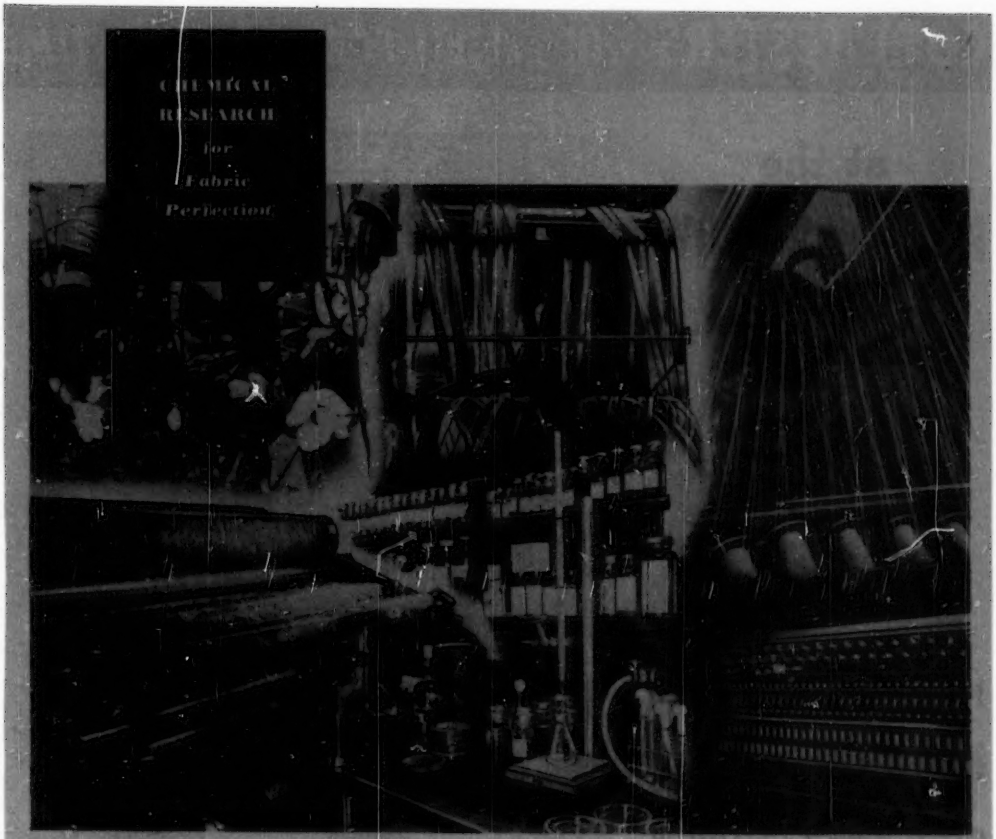

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TEXTILE RESEARCH JOURNAL

VOL. XIX, NO. 3 March, 1949

Dynamic Properties of Filaments, Yarns, and Cords at Sonic Frequencies*

W. James Lyons

Chemical and Physical Research Laboratories, The Firestone Tire and Rubber Company, Akron, Ohio

Abstract

A brief description of the stretch-vibrometer developed at the Firestone Research Laboratories is given, and the theory of its operation is outlined. Described are new measurements made on the instrument verifying the previous conclusion that loss of energy to the apparatus is immeasurably small. Values of the dynamic stretch moduli E, coefficients of internal friction μ, and hysteretic energy losses of 15 samples of natural and synthetic textile materials, Fiberglas, and steel wire are given. Corresponding static values of moduli and energy losses are also given. The latter, it is shown, do not correlate with dynamic values, and hence cannot be regarded as predictive of dynamic behavior. The resonant frequencies at which measurements were made on these samples ranged from 65 to 360 cycles per second.

The significance of the various measures which have been employed with the present data to express hysteretic losses is discussed, and it is shown that the quantity $\mu\omega_0/E$, while not rigidly constant, is confined to a narrow range of values in most samples. Further evidence is submitted generalizing the near-hyperbolic relationship between μ and ω_0. Results of application of the method to the comparison of various tire-cord rayons are given. Measured on the stretch-vibrometer have been dynamic moduli ranging from 2.1×10^{10} (rubber thread) to 226×10^{10} (steel wire) dynes/cm.^{2}, and internal-friction coefficients from 0.74×10^6 (rubber thread) to 25.7×10^6 (silk thread) poises.

BY THE "DYNAMIC PROPERTIES" of a material (usually considered in the solid, or colloidal state) is understood its modes of response while being continuously loaded or unloaded at an appreciable rate. The dynamic properties of a textile element, such as a filament or cord, without reference to the molecular structure of which these properties are functions, directly determine the serviceability of these elements in mechanical applications, such as tire and fan-belt fabrics. Indirectly, however, dynamic properties also have implications in the behavior of textile materials in applications where the conditions are essentially static, but involve elasticity and resilience [4]. At the molecular level these latter properties are closely bound up with the dynamic properties. Into the nature of molecular forces and structure which define all gross properties, a knowledge of the dynamic properties of a material, textile or any other, provides an insight which goes beyond that which can be obtained from conventional static measurements alone. As a matter of fact, the first dy-

* The material in this paper was presented at the Gordon Research Conference on Textiles of the American Association for the Advancement of Science, New London, N. H., July, 1948.

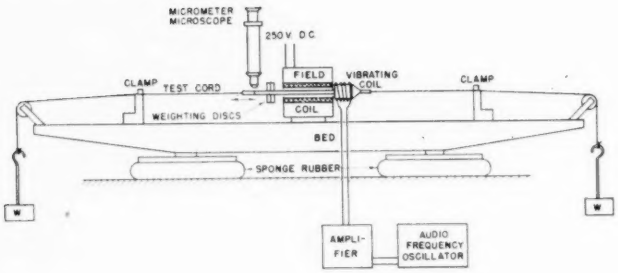

FIG. 1. *Schematic diagram of stretch-vibrometer and auxiliary equipment.*

namic measurements made on textile fibers, those of Meyer and Lotmar [8], were applied not to ascertaining the suitability of certain fibers for dynamic applications but to the structural analysis of the cellulose network.

Generally, in the laboratory measurement of dynamic properties the loading is in regular cycles and of sinusoidal form, at frequencies from the low acoustic up into the ultrasonic. The first researches on textiles [2, 8] were limited to measurements of a single dynamic property: the stretch modulus (Young's). As is attested by the amount of work which has been done in the fields of metals and rubber, there are other dynamic properties which have considerable interest. Measurements of two of these, the coefficient of internal friction and hysteretic energy loss, as well as of the stretch modulus, have been included in the present investigations.

Method

The stretch-vibrometer and the method employed have been previously described in some detail [7]. A schematic diagram of the apparatus is shown in Figure 1. Briefly, the method consists of passing a small oscillating current of known frequency through a coil which rests in the field of a strong electromagnet and which is supported coaxially by two equal lengths of the test string, which are necessarily under tension. The passage of the current through the coil causes it to vibrate axially, thus alternately elongating and relaxing the specimens of string. The amplitude of vibration is measured by means of a micrometer microscope focused on a mark on the vibrating system. The stretch-vibrometer has been so calibrated that for a given length of sample (usually 25.4 cm.) readings of the vibrating-coil current, its frequency, and the amplitude of vibration provide the necessary data from which the desired dynamic parameters can be calculated. Measurements are made at resonance. Typical extremes in amplitude of vibration are 0.080 cm. (0.3 percent) for a nylon cord, and 0.010 cm. (0.04 percent) for glass cord.

Underlying the present method is the equation of motion of the vibrating-coil system:

$$m\frac{d^2s}{dt^2} + \left(\frac{\mu}{q} + J\right)\frac{ds}{dt} + \frac{E}{q}s = F\cos\omega t, \qquad (1)$$

where m = vibrating mass; s = displacement from equilibrium position; μ = coefficient of internal friction in the test specimen; q = shape factor of specimen; J = coefficient of instrumental damping; E = dynamic stretch modulus; and F = amplitude of applied force having frequency $\omega/2\pi$. A series of measurements have disclosed that the energy loss to the instrument is negligible, and that hence $J = 0$. Accepting this condition, the solution of equation (1) leads to the following formulas for the dynamic properties:

$$\text{dynamic modulus, } E = qm\omega_n^2, \qquad (2)$$

$$\text{coefficient of internal friction, } \mu = \frac{qF}{s_m\omega_n}; \qquad (3)$$

$$\text{total energy loss per cycle, } H = Fs_m\pi; \qquad (4)$$

$$\text{hysteretic constant (energy loss per cycle per unit volume), } H_v = \mu s_m^2\omega_n\pi/L^2 \qquad (5)$$

$$= Fs_m\pi/2AL. \qquad (6)$$

The quantity ω_n represents the resonant value of ω, while s_m is the maximum amplitude (at resonance). L is the length of one of the specimens and A is the cross-sectional area.

Energy-Loss Functions

Since the energy loss, according to equation (5), is a function of the strain-amplitude s_m/L, it evi-

dently depends upon particular experimental conditions, and is not a parameter characteristic of the material. To obtain a quantity which is more nearly a material constant, the energy loss per unit strain-amplitude has been computed for the various samples studied. The energy loss per unit strain-amplitude is evidently the hysteretic constant H_c for $s_m/L = 1$, and thus is given by the expression $\mu\omega_o\pi$. By referring energy losses to a uniform strain-amplitude, comparison may be made between materials tested with different strains. The result, under ideal conditions, will give the same proportionate energy losses among the materials as they would if they had been tested at the same strain-amplitude. Because it is found experimentally that even energy losses referred to unit strain-amplitude are not, in general, strictly independent of strain-amplitude itself, the amplitude range should not be too wide.

There are many cases in which it is not practical to compare materials on the basis of uniform strain-amplitude, for in actual service they would experience widely different strains because of their different dynamic properties. This is particularly true of the mechanical fabrics, since they are the load-supporting structures in the products of which they are a part. Thus if, in a tire of a given type and size, one textile material is replaced by another approximately cord-for-cord, the two samples would experience cycles of nearly uniform stress-amplitude. For applications of this type it is advantageous to make comparisons in terms of energy loss per unit stress-amplitude. This quantity, like that referred to unit strain-amplitude, varies with strain-amplitude.

Defining the dynamic stretch modulus E as the ratio of instantaneous elastic stress to instantaneous strain, as implied by the presence of the term $(E/q)s$ in equation (1), we have

$$\text{elastic stress} = \frac{Es}{L}. \qquad (7)$$

For unit stress-amplitude, $Es_m/L = 1$. Referring to equation (5), it can be readily verified that H_c/unit stress-amplitude, the energy loss per unit stress-amplitude, is given by the expression $\frac{\mu\omega_o\pi}{E^2}$.

Another quantity which has been used to evaluate hysteresis in vibration processes is the "loss-angle tangent," introduced into mechanical problems by analogy with the behavior of oscillatory electric currents, in the theory of which the term appears to have been used first. The loss-angle tangent is a dimensionless quantity given by the expression $\mu\omega_o/E$. As is indicated in the Appendix, in which its significance is discussed, the quantity $\mu\omega_o/E$ does not measure energy loss but is directly dependent upon the intrinsic frictional resistance of the material. Values of the loss-angle tangent have been calculated for a number of materials on which results are herein given.

The moduli, frictional coefficients, and energy losses computed from vibrometer data on samples in the form of yarns or cords evidently reflect the influence of gross construction as well as of molecular structure. The properties of the latter alone are given by tests on monofils. The measurement of parameters which involve construction is useful where construction itself is under study or where the aim is to evaluate the dynamic performance of a finished textile product, as, for instance, a twisted and stretched tire cord.

Instrumental Energy Losses

In the original publication on the present model of the stretch-vibrometer [7] there were described measurements, with cotton cord in the apparatus, from which it was found that energy absorption (damping) by the instrument was indetectably small. With a view to securing further and more refined verification of this finding it was decided to conduct measurements on materials which in themselves have lower total damping-energy losses than has cotton cord. Accordingly, experiments were conducted with nylon and steel monofils.

As has been shown, the total damping energy per cycle lost to the system, including the instrument, can be calculated by means of an equation analogous to equation (4). The part of this energy which is dissipated in the vibrating string is presumably directly proportional to the length of the string. It would be supposed that at a given frequency the loss to the instrument would be constant. Thus, if total energy losses are measured for various lengths of the string, and are extrapolated to zero length of string, the residual would be the instrumental energy loss. On a plot of total damping energy *vs.* specimen length, the energy-intercept would be the instrumental loss.

The results of the present experiments with nylon and steel are shown in Figures 2–5. Measurements were made on the nylon at eight different lengths, as indicated in Figure 2. It will be seen that the

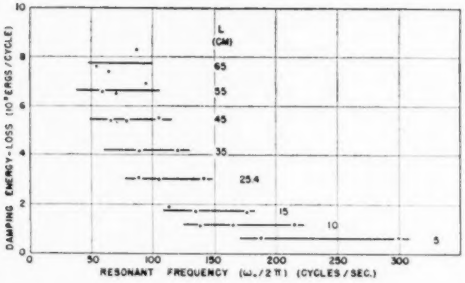

FIG. 2. *Total damping energy loss per cycle, in whole vibrating system, with high-tenacity nylon monofil in vibrometer, various lengths L of specimen being used.*

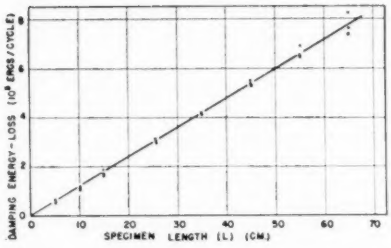

FIG. 3. *Linear dependence of damping energy loss of nylon monofil on specimen length; from data of Figure 2.*

energy losses are substantially independent of frequency in the ranges covered. The mean energy losses are plotted against specimen lengths in Figure 3. The tests on the steel wire were more difficult to make with accuracy because of the small forces involved and the difficulty in reading the stress-amplitude at resonance, which was very sharp with this material. Measurements were made with an impressed force-amplitude of 1,080 dynes and then with half of this force in order to secure more stable operation. The results are shown in Figure 4. While mean energy losses for each specimen length were used in plotting Figure 3, values interpolated for a single frequency (180 c.p.s.) were used in Figure 5, since the energy-loss data seemed to indicate the possibility of frequency-dependence in this case. It should be noted that the scale of the damping energy loss in Figures 4 and 5 for the steel wire is smaller by a factor of about 100 than that for the nylon monofil.

The results on the nylon qualitatively duplicate those obtained previously with cotton cord. Both sets of data confirm the earlier deductions that (*a*) the energy loss/cycle in the specimen string is directly proportional to the length, and (*b*) the stretch-vibrometer itself absorbs no sensible amount of energy.

Another point, interesting because it enhances the credibility of the method, is that the graph for $F = 540$ dynes in Figure 5 gives nearly one-fourth the energy loss at any particular value of L as does the graph for $F = 1{,}080$ dynes, as required by the relationship:

$$H = \frac{qF^2\pi}{\omega_0\mu}. \qquad (8)$$

This equation follows necessarily from equation (4) and from the solution at resonance, s_m, of equation (1).

Results

1. Comparison of Dynamic and Static Properties

In Table I are given the dynamic stretch moduli of 15 samples of textiles, Fiberglas, and steel wire, in the order of descending values of the moduli. Each value of E is an average based on a set of at least three observations with different vibrating masses and specimen lengths. A uniform tensional load of 2.0 kg. was applied to all samples except the steel cord, on which a 2.9-kg. load was used.

Loading and unloading curves (at least two loops) were obtained on a Scott incline-plane serigraph, Type IP-4, on the 15 samples, after conditioning at 55% R.H., 75°F. The maximum load in all cases, except that of the steel wire cord, was 10 lb. For the yarns and monofils, sufficient parallel strands were tested to produce total cross-sectional areas equal to those used in the dynamic tests and, accordingly, comparable to those of the tire cords. Values of the static moduli calculated from the mean slope of the loading and unloading curves of the second loop are given in Table I for comparison with the corresponding dynamic moduli.

It will be observed that for all samples except the steel monofil the ratio of dynamic to static modulus (see Table I) is substantially greater than unity. This may be interpreted as indicating that during the slow static loading, quasi-elastic, if not plastic flow occurs, thus contributing to the observed elongation corresponding to a given load. The computed static modulus is thus smaller than it would be were this contribution absent. In the dynamic test, there is insufficient time for the flow and orientation of the molecules of the filaments or

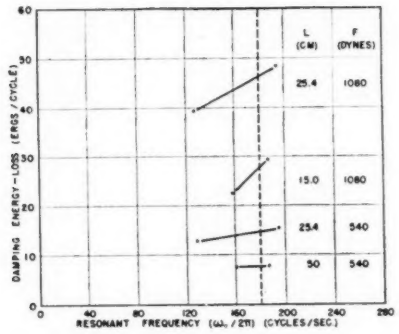

FIG. 4. *Total damping energy loss per cycle with 2 different lengths of 6-mil steel music wire in vibrometer. Two amplitudes of impressed force* F *were used with each length of specimen.*

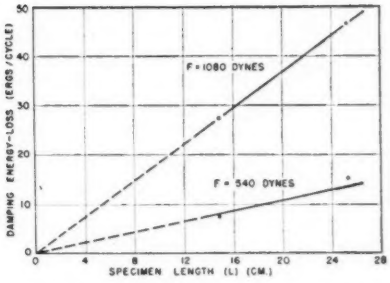

FIG. 5. *Linear dependence of damping energy loss of steel wire on specimen length and amplitude of impressed force; from data of Figure 4.*

for the rearrangement and shift of the fibers and filaments of yarns and cords before the applied force is reversed. The more plastic the material, the greater the ratio of dynamic to static modulus. Thus for the steel monofil, for which, in this static test, there was little opportunity for plastic flow, the ratio is a minimum, while for the newer synthetic organic filaments—Fiber A, Vinyon N, and Velon—which exhibit pronounced elongation in standard creep experiments, the maximum ratios are found. The role played by plastic flow in determining the ratios of dynamic to static moduli for various filament samples is eloquently shown by comparing the ratios for Vinyon N, nylon, and rayon yarns in Table I with the creep of these yarns, as depicted in Figure 6. On this graph rayon, with a ratio of 1.86, has the least creep, while Vinyon N, with a ratio of 2.41, has the greatest creep, nylon (ratio = 2.04) being intermediate in creep.

In Table II are listed the coefficients of internal friction μ of 14 of the samples in Table I, and in the same order. The internal-friction coefficients of many of these samples, as functions of resonant frequency, were presented graphically in Figure 7 of the previous publication on the stretch-vibrometer [7]. The values of μ are those interpolated for 180 c.p.s., from values calculated for at least two other resonant frequencies at which observations were actually made. Also tabulated are loss-angle tangents, $\mu\omega$, E_d, dynamic energy loss per unit strain-amplitude, and the dynamic energy loss per unit stress-amplitude, all derived from the E and μ values given in Tables I and II.

Included in Table II are the *static* energy losses per unit strain-amplitude and per unit stress-amplitude for the 12 strictly textile samples. The former was calculated from the area of the second hysteresis loop of the serigraph chart of the particular sample, using the formula:

$$\frac{2.26 \times 10^6 \times \alpha \times \lambda}{A \times L \times \Delta\lambda} \text{ ergs},$$

where 2.26×10^6 is the number of ergs represented by each square inch on the chart; α is the area of hysteresis loop (in.^{2}); λ is the mean unloaded length of specimen for the second loop; $\Delta\lambda$ is the mean elongation on full loading during the second cycle; A and L are the initial area and length of the specimen, respectively.

The static loss per unit stress-amplitude was obtained from the expression:

$$\frac{\text{Energy loss per unit strain-amplitude}}{E_s^2},$$

where E_s is the static (Young's) modulus given by the same loop, as listed in Table I.

It will be seen that not only are the dynamic and static energy losses, on either basis, in general, of different orders of magnitude but they also assume different relative proportions and even different ranks in corresponding columns. With the exception of those for one or two samples, the data based on unit stress-amplitude show a tendency to correlation between the groups of low values and those of high values. It is probable that repeated cyclic stressing in the static experiment would improve the correlation of data on some of the poorly oriented filaments. In general, however, the static energy losses are not reliable indicators of relative dynamic

TABLE I. DYNAMIC MODULI OF CORDS, YARNS, AND MONOFILS COMPARED TO STATIC MODULI (TEMPERATURE RANGE: 21°–25°C)

Material	Description of sample: Construction	Cross-sectional area (cm.²)	Stretch modulus (10^{10} dynes/cm.²): Dynamic E	Stretch modulus (10^{10} dynes/cm.²): Static (2nd loop)	Ratio of dynamic to static modulus	Static tension on specimen (kg./mm.²)
Steel	Monofil; 6-mil	0.00018	213	203	1.05	112.8
Steel	6 × 3 × .0058-in. cord	.0036	106	83	1.28	8.1
Fiberglas	7-ply cord	.0026	53.9	26.2	2.06	7.8
Ramie	3-ply cord	.0018	31.9	22.2	1.44	11.3
Rayon (viscose)	1,100-den. yarn (2 strands)	.0016	19.7	10.6	1.86	12.7
Fiber A (du Pont)	300-den. yarn (6 strands)	.0017	16.4	6.1	2.69	11.9
Rayon (viscose)	1,100/2 cord	.0018	15.2	7.4	2.06	11.3
Fiber V (du Pont)	75/16/2 cord	.0022	10.9	6.4	1.70	9.2
Vinyon N	300-den. yarn; Type NORU (6 strands)	.0016	10.6	4.4	2.41	12.7
Cotton	11/4/2 cord	.0032	10.2	4.6	2.22	6.4
Nylon	210-den. yarn (9 strands)	.0018	9.8	4.8	2.04	11.3
Nylon	210/3/3 cord	.0019	8.7	3.9	2.23	10.7
Nylon (high-tenacity)	Monofil (2 strands)	.0024	8.0	4.3	1.86	8.5
Velon	Monofil (3 strands)	.0021	6.4	2.3	2.78	9.7
Nylon	Monofil; 12-mil (3 strands)	.0020	6.0	2.6	2.31	10.1

losses as observed by the present stretch-vibrometer method. Scatter diagrams are shown in Figure 7, graphically demonstrating the lack of correlation between energy losses determined statically and those determined dynamically.

The loss-angle tangent $\mu\omega/E$ would be expected to vary only slightly with frequency. As has been already noted [7], $\mu\omega$ is roughly a constant for a particular sample. Also, as has been demonstrated quite thoroughly with respect to cotton cord and nylon monofil over the frequency range employed in the present work, the modulus E is independent of frequency. How well this expectation is fulfilled by the present results is shown in Table III,

TABLE II. HYSTERETIC PROPERTIES OF CORDS, YARNS, AND MONOFILS (TEMPERATURE RANGE: 21°–25°C)

Material	Description of sample: Construction	Dynamic properties at 180 c.p.s.: Internal friction μ (10^6 poises)	Loss-angle tangent (dynamic) $\mu\omega/E$	Energy loss: Per unit strain amplitude (10^{10} ergs/cycle/cm.³)	Energy loss: Per unit stress amplitude (10^{-12} ergs/cycle/cm.³/(dynes/cm.²)²)	Static Energy loss: Per unit strain-amplitude (10^{10} ergs/cycle/cm.³)	Static Energy loss: Per unit stress-amplitude (10^{-12} ergs/cycle/cm.³/(dynes/cm.²)²)
Steel	Monofil; 6-mil	6.2	0.0033	2.22	0.0048	(immeasurably small)	
Fiberglas	7-ply cord	11.3	.024	4.00	.14	(immeasurably small)	
Ramie	3-ply cord	7.5	.027	2.66	.26	0.058	0.012
Rayon	1,100-den. yarn (2 strands)	4.9	.028	1.74	.45	.088	.077
Fiber A (du Pont)	300-den. yarn (6 strands)	8.9	.061	3.16	1.18	.110	.292
Rayon	1,100/2 cord	4.0	.030	1.42	.62	.090	.162
Fiber V (du Pont)	75/16/2 cord	3.1	.032	1.10	.92	.061	.150
Vinyon N	300-den. yarn; Type NORU (6 strands)	4.1	.044	1.46	1.30	.140	.709
Cotton	11/4/2 cord	5.2	.058	1.85	1.78	.057	.275
Nylon	210-den. yarn (9 strands)	3.1	.036	1.10	1.15	.050	.221
Nylon	210/3/3 cord	2.3	.030	0.82	1.08	.036	.239
Nylon	Monofil; high-tenacity (2 strands)	2.3	.033	0.82	1.28	.038	.276
Velon	Monofil (3 strands)	10.0	.176	3.55	8.66	.033	.604
Nylon	Monofil; 12-mil (3 strands)	2.7	.051	0.96	2.67	.047	.719

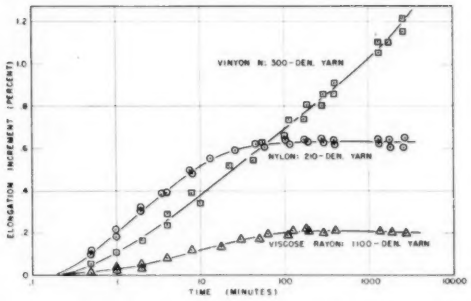

FIG. 6. *Creep of yarns of synthetic filaments at 50°C, with uniform loads of 3.78 kg./mm.² (5,380 p.s.i.).*

wherein the extreme spreads in the loss-angle tangents of our 14 samples are given. It will be seen that the loss-angle tangent tends to remain near a constant value but that in only a few cases are the results concordant, with the theory that $\mu\omega_0 E$ is an exact constant. In general, however, the range of loss-angle tangent values is much smaller proportionately than the frequency range. It should be noted that the extremes of the frequency and loss-angle tangent ranges are not always coincident, so that from these data the systematic increase or decrease of the loss-angle tangent with frequency cannot be deduced.

2. Reproducibility

In Table IV is given the statistical analysis of results on 6 specimens of a single sample of rayon cord, successively mounted in the stretch-vibrometer. The variation here could be due conceivably to variations in experimental technique as well as to non-uniformity in the sample. Since, however, measurements repeated on single specimens mounted in the apparatus are reproducible to the

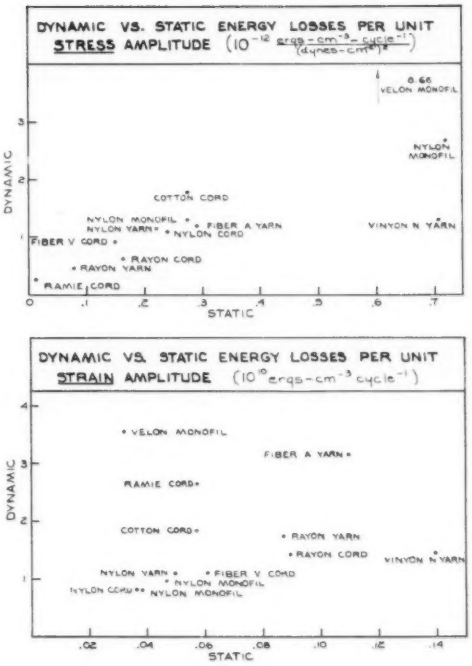

FIG. 7. *Comparison of energy losses obtained from dynamic measurements with those obtained by the static method employing the incline-plane tester.*

TABLE III. EXTREME SPREADS IN LOSS-ANGLE TANGENT OF VARIOUS CORDS, YARNS, AND MONOFILS, RESULTING FROM VARIATIONS IN RESONANT FREQUENCY AND OTHER EXPERIMENTAL CONDITIONS

Sample description	Frequency range (c.p.s.)	Range of loss-angle tangent
Steel monofil; 6-mil	128–195	0.0027–.0045
Fiberglas cord	232–359	.0262–.0298
Ramie cord	154–231	.0250–.0291
Rayon, 1,100-den. yarn	114–225	.0259–.0303
Fiber A (du Pont) yarn	105–165	.0607–.0647
Rayon, 1,100/2 cord	99–160	.0297–.0310
Fiber V (du Pont) cord	95–155	.0276–.0298
Vinyon N yarn; Type NQRU	81–129	.0470–.0493
Cotton cord	68–309	.0540–.0695
Nylon yarn	100–170	.0344–.0370
Nylon cord	79–127	.0262–.0287
Nylon monofil; high-tenacity	65–300	.0275–.0340
Velon monofil	72–115	.1648–.1708
Nylon monofil; 12-mil	67–109	.0545–.0563

TABLE IV. ANALYSIS OF TESTS ON REPLICATE SPECIMENS OF A SINGLE SAMPLE OF 2,200/2 RAYON TIRE CORD (MEAN FREQUENCY: 136.8 C.P.S.)

	Dynamic modulus (10^{10} dynes/cm.²)	Coefficient of internal friction (10^6 poises)
Individual observations		
Test 1	13.7	4.81
Test 2	13.4	4.85
Test 3	13.5	4.88
Test 4	13.35	4.86
Test 5	13.4	4.86
Test 6	13.65	4.77
Average value	13.50	4.84
Standard deviation	0.132	0.0376
Coefficient of variation (%)	0.98	0.78

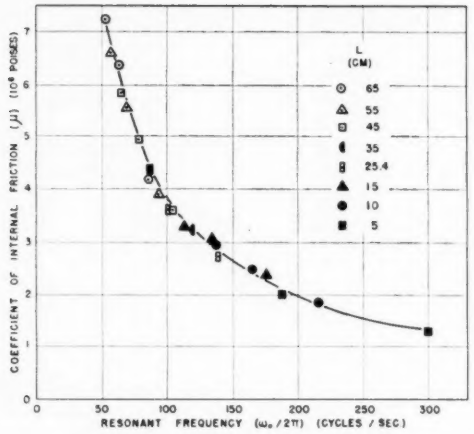

FIG. 8. *Coefficient of internal friction of high-tenacity nylon monofil, showing strong dependence on resonant frequency; for eight different specimen lengths.*

limits of precision of observation, the evidence inclines toward the conclusion that most of the variation disclosed by Table IV is due to non-uniformity in the sample.

From the data in Table IV, an energy loss/unit strain-amplitude of 1.31×10^{10} ergs/cycle/cm.^{3} and an energy loss/unit stress-amplitude of 0.72×10^{-12} ergs/cycle/cm.^{3}/(dynes/cm.^{3})^2 are calculated. Comparing these results with those for 1,100/2 rayon in Table II, it will be seen that, despite differences in sample construction and the frequency of measurement, the energy-loss values for high-tenacity rayon cords lie within a rather narrow range.

3. *Temperature Rise in Cotton Cord During Measurements on Stretch-Vibrometer*

The experiments on the stretch-vibrometer have established the occurrence of hysteretic energy losses, according to dynamical theory. Considerations of energy conservation indicate that these losses represent generated thermal energy, but no direct measurement of heat as such is involved in the regular use of the vibrometer. Because of the nature of the test specimens no reasonably accurate measurement of quantity of evolved heat is feasible. The evolution of heat on the vibrometer is so slow that the conditions are nearly isothermal. It was recognized, however, that a small rise in temperature might occur in a test cord or yarn, since textile materials are not good heat conductors.

To determine whether the observed loss of mechanical energy (hysteresis), converted to thermal energy, was detectable as a temperature rise, measurements were made by means of an iron-constantan thermocouple inserted between the plies of a 14/3/3 cotton cord. Very fine wires (No. 36 B and S gage) were used. Standard test conditions were employed (2,033 g. static tension, 29.3 g. impressed force), with a strain-amplitude of 0.084 percent.

Under these conditions a temperature rise of 0.3°C was reached in less than 1 minute and was held for 7 minutes. A corresponding temperature drop was found upon cessation of operation.

The temperature rise of only 0.3°C in the cotton cord in this experiment indicates that the thermal effect was not entering as a relevant variable in the vibrometer experiments. The strain-amplitude is estimated to be smaller than that in a tire cord in service by an order of magnitude. Furthermore, with the specimens in the vibrometer exposed to air in motion (promoting near-isothermal conditions) the heat losses would be expected to be greater than they would be in a tire, where the cords are imbedded in poorly conducting rubber. In spite of the rather negligible temperature rise observed in this experiment, full consideration of all the factors leaves open the possibility that, because of cumulative effects, a significant contribution may be made by the fabrics to heat build-up in tires.

4. *Internal Friction of Nylon and Steel Monofils*

The considerable amount of data obtained on the nylon and steel wire in verifying the instrumental-loss features of this method, as described in a fore-

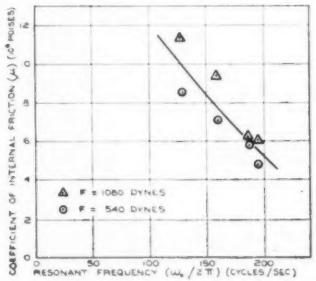

FIG. 9. *Coefficient of internal friction of steel wire, showing frequency dependence; two amplitudes of impressed force F were used.*

TABLE V. EFFECT OF "SLASHING" PROCESS ON DYNAMIC AND OTHER PHYSICAL PROPERTIES OF 1,100/2/2 RAYON TIRE CORD

Property		Unslashed rayon	Slashed rayon
General	Specific		
Dynamic (207–217 c.p.s.; 24°C, 55% R. H.; 2,940 g. static load)	Stretch modulus (10^{10} dynes/cm.^{2})	13.8	16.4
	Energy loss		
	per unit strain-amplitude (10^{10} ergs/cycle/cm.^{3})	1.34	1.50
	per unit stress-amplitude (10^{-12} ergs/cycle/cm.^{3}/(dynes/cm.^{2})^2)	0.70	0.56
Creep (140°C; 2,268 g. static load)	Elongation increment		
	0.2 to 10 min. (%)	1.20	0.74
	0.2 to 100 min. (%)	2.00	1.15
	0.2 to 1,000 min. (%)	2.60	1.50
Tensile	Conditioned (24°C, 55% R.H.)		
	Breaking load (lb.)	31.2	31.1
	Elongation at 20 lb. (%)	13.3	6.7
	Elongation at 30 lb. (%)	20.5	11.4
	Oven-dried		
	Breaking load (lb.)	35.7	35.2
	Elongation at 20 lb. (%)	4.6	4.0
	Elongation at 30 lb. (%)	11.5	7.5

going section, provided the means of examining in detail the dependence of the coefficient of internal friction upon resonant frequency, for these materials. In Figures 8 and 9 are plotted the coefficients of internal friction of the nylon and steel monofils as functions of resonant frequency. The experimental points for the nylon conform very gratifyingly to the hyperbolic law relating internal friction and frequency. In Figure 9 the points are more scattered, those for a force-amplitude of 1,080 dynes tending to form one locus, and those for 540 dynes tending to form another. This condition, as well as the fact that in Figure 5 the graph for $F = 540$ dynes lies slightly higher than theory would dictate, would appear to indicate* that the mean observed values of the displacement-amplitude at resonance, when $F = 540$ dynes, were slightly too large, or when $F = 1{,}080$ dynes, slightly too small, for exact concordance with theory.

5. Typical Studies with the Stretch-Vibrometer

(*a*) In Table V are compared the dynamic properties of a rayon tire cord, in the manufacture of which the "slashing" process had been omitted, with those of a slashed control cord from the same supplier.† Also included in Table V are data on creep and conventional tensile properties. That slashing, recognized as an orienting process, produces a stiffer cord is shown by the higher modulus of the slashed cord, even under a 3-kg. (6½-lb.) load. Because the unslashed rayon is softer or more compliant, it will do more "working" in a tire in which it replaces a slashed rayon, cord-for-cord. Because the internal friction is not sufficiently good in the unslashed cord, the more active working results in greater heat generation, as is implied by the fact that for the unslashed cord the energy loss/unit stress-amplitude is over 40 percent higher than for the slashed cord. The increased stiffness or rigidity of the slashed cord is reflected also in the reduction in its creep rate and in its extensibility in the tensile tests.

TABLE VI. DYNAMIC PROPERTIES OF RAW RAYON TIRE CORDS FROM VARIOUS SUPPLIERS (STATIC TENSION: 2.94 kg.)

Supplier	Construction	Cross-sectional area (cm.^{2})	Dynamic modulus (10^{10} dynes/cm.^{2})	Coefficient of internal friction (10^6 poises)
I	2200/2	.00352	13.5	4.84
II	2200/2	.00340	14.6	4.59
I	1100/2/2	.00354	13.1	4.68
III	1100/2/2 Type A	.00353	13.4	4.53
III	1100/2/2 Type B	.00355	12.7	4.86
IV	1100/2/2	.00342	13.7	4.52

* *Cf.* reference [7], equations (12) and (14).

† The modulus and conditioned breaking load of the control suggest that the original yarns in these cords were not of regular type.

TABLE VII. COMPARISON OF DYNAMIC PROPERTIES OF WIDELY DIVERSE FILAMENTOUS MATERIALS

Description of sample	Dynamic stretch modulus (10^{10} dynes/cm.^{2})	Coefficient of internal friction (10^6 poises)	Frequency (cycles/sec.)	Energy loss: Per unit strain-amplitude (10^{10} ergs/cycle/cm.^{3})	Energy loss: Per unit stress-amplitude (10^{-12} ergs/cycle/cm.^{3}/(dynes/cm.^{2})^2)
Steel music wire monofil; 6-mil (0.0152 cm.) di., 0.00018 cm.^{2} cross section	226	10.0	128	2.84	0.0056
Viscose rayon; 1,100-den. yarn; 2 strands; 0.0016 cm.^{2} cross section	19.7	4.9	180	1.74	0.45
Silk sewing thread; approx. 210 den.	15.6	25.7	185	1.50	0.62
Wool yarn; 100% 8-ply; approx. 4,100 grex	5.2	21.6	110	0.74	2.76
Natural rubber golf-ball thread; 900% elongation	2.12	0.74	65	0.09	2.10

(*b*) Rayon cords of 2,200/2 or equivalent construction from four suppliers were compared on the basis of dynamic properties, with the results shown in Table VI. On the basis of the uniformity test covered by Table IV, it can be concluded that many of the differences in Table VI are real, and that different lots of rayon cord which are presumably replicates do in fact differ in dynamic properties. It is believed, however, on the basis of other additional evidence, that differences just as large are found between different lots from the same supplier.

(*c*) One of the most recent accomplishments in the development of the stretch-vibrometer method has been a technique adapting it to measurements on polymers exhibiting superelasticity. In Table VII dynamic results obtained with the stretch-vibrometer on a natural rubber thread are given, along with those on other filamentous materials having widely different properties. It is of interest to note that, in comparison with the value of 226×10^{10} dynes/cm.^{2} for the modulus of the steel wire in Table VII, H. N. Davis [3] in 1906 found a value of 229×10^{10} dynes for Young's modulus in a longitudinal-vibration experiment on a 0.4-mm. steel wire. He used a mechanically driven apparatus.

How well viscose rayon functions as an artificial silk (its original role) is indicated roughly by comparison of the dynamic moduli and energy losses of the two materials. The low value of the dynamic modulus of the wool yarn in Table VII supports the idea that, in the region of small deformations, wool behaves as a rubber.

Acknowledgment

The accumulation of the experimental data cited in the present report has been the work of Mr. Irven B. Prettyman, whose skillful operation of the apparatus and careful, though numerous, computations have accelerated the progress of this development. The cooperation of the officials of the Firestone research organization in making possible this contribution is gratefully acknowledged.

Appendix

Theoretical Model and Electrical Analog of the Vibrometer System

A clearer understanding of the significance of the experiments and results of the present researches will be afforded by a consideration of the simplified mechanical model which represents the vibrating system. An outline of the analogy between this model and an electrical circuit also will be of interest, for the implications of many electrical quantities are more familiar to physical scientists than are those of their mechanical counterparts. In the present discussion, the significance of the loss tangent $\mu\omega_n/E$, in particular, as a measure of hysteresis loss, will be brought out by the electrical approach. The electrical analogy has further interest because of the possibility that corresponding mechanical and electrical properties are directly related at the molecular level and are simply differently observed manifestations of the same elementary process. The frequency range in which these relationships are likely to hold, however, is much above that of the present experiments.

We note that the terms on the left-hand side of the equation of motion, equation (1), may be separated into the *kinetic reaction* $m\frac{d^2s}{dt^2}$ of the vibrating element, and the *structural forces* $\frac{\mu}{q}\frac{ds}{dt} + \frac{E}{q}s$. The latter, representing the dynamic response of the test specimen, contains the quantities which we wish to evaluate. In the structural-force expression, the coefficient of instrumental damping, J, which we have found to be substantially zero, is neglected. The structural forces are seen to be those of a Voigt model, shown in Figure 10(*a*). It should be noted, however, that while the Voigt model and the structural terms in equation (1) are in good conformity with each other, they are simplified representations of the combination of numerous mechanical systems of which the high polymeric specimens are supposed to consist. Presumably a much better, but mathematically unmanageable, approximation to the perfect representation would be given by an ensemble of various models and inertial elements with a distribution of values of E, μ, and m. The values of these parameters which are derived by the present method are to be regarded as effective averages. With this limitation on the significance of the parameters, their interpretation with the aid of the electrical analogies may be considered.

By a well-known rule of analogy between mechanical and electrical systems [1], the parallel coupling of elastic and viscous elements in the Voigt model transforms into the series coupling of resistance r and capacitance c in an electrical circuit, when the dependent variables are displacement and electrical charge, respectively. The electrical circuit corresponding to the vibrometer system is shown in Figure 10(*b*). The circuit contains inductance l, as well as resistance and capacitance, and the complete voltage relationships are

$$l\frac{d^2Q}{dt^2} + r\frac{dQ}{dt} + \frac{Q}{c} = V\cos\omega t. \quad (9)$$

By reference to the table of analogs in Figure 10, it will be seen that this equation is completely analogous to equation (1), for $J = 0$.

At resonance in this circuit, when, to a very good approximation for usual, small values of r, $\omega_o = \sqrt{1/lc}$, the current (rate of charge displacement) and the voltage are in phase. If, however, the circuit contained no inductance, consisting only of the r and c part in Figure 10, it could never be brought to resonance. The current would lead the voltage in phase by varying degree, depending upon the resistance of the circuit and the frequency. The phase-angle tangent for this case is

$$\tan\phi_{\text{elec}} = \frac{1}{rc\omega}. \quad (10)$$

For a perfect condenser having no dielectric losses and $r = 0$, $\tan\phi_{\text{elec}} = \infty$, and $\phi_{\text{elec}} = 90°$.

It will be seen that as r increases the angle of lead ϕ_{elec} decreases, and thus the amount by which ϕ_{elec} decreases below 90° may be taken as a measure of the dielectric ohmic losses in the condenser, and the resistance of the connections and remainder of the circuit, all represented by r. Hence, the *angle of loss* or *phase displacement* is $\theta_{\text{elec}} = 90 - \phi_{\text{elec}}$, and the loss-angle tangent is

$$\tan\theta_{\text{elec}} = rc\omega. \quad (11)$$

In an inductive circuit, the phase displacement which tends to arise because of ohmic losses in the capacitative section is offset by the effect of the l, so that the net phase displacement ceases to be a measure of energy dissipation. However, if the quantities r, c, and l are known, the loss tangent

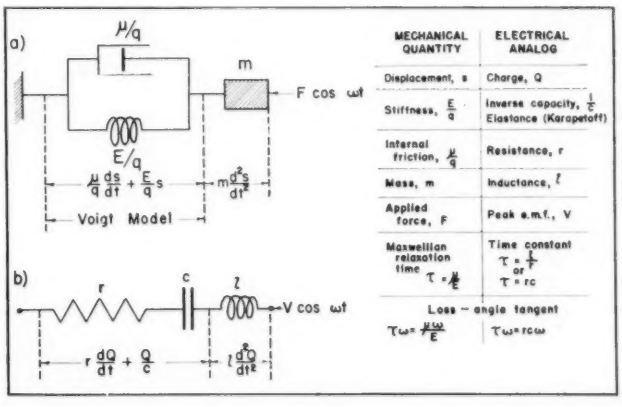

FIG. 10. *Idealized mechanical model of vibrometer system, with equivalent electrical network.*

can be calculated by equation (11), even though the computed quantity has no physical counterpart in the particular experiment. The quantity rc will have real significance as a relative measure of energy dissipation.

Correspondingly, at resonance in the present mechanical experiments, we have taken $E = qm\omega_o^2$, or $\omega_o = \sqrt{\frac{E}{qm}}$, which is analogous to $\sqrt{1/lc}$.* The rate of displacement $\frac{ds}{dt}$ and the applied force are in phase, while the displacement s lags behind by 90°. The phase angle ϕ in equation (1) can be seen, by considering its function in that equation, to represent the amount by which the displacement s, rather than the rate of displacement, lags behind F in phase. The phase-angle tangent is

$$\tan \phi = \frac{\mu\omega}{E - qm\omega^2}, \quad (J = 0). \tag{12}$$

At resonance, $E = qm\omega_o^2$, $\tan \phi = \infty$, and $\therefore \phi = 90°$. The phase angle ϕ, as defined and used above for the mechanical case, differs from ϕ_{elec} by 90°. In the mechanical problem the phase angle refers to the lag of the dependent variable (in the original equation of motion), whereas in the electrical case phase angle has been accepted to mean the lag of the *time-rate of change* of the dependent variable behind the force agency. For these reasons $\tan \phi$ in equation (12) is the inverse of its electrical analog, $\frac{\frac{1}{c\omega} - l\omega}{R}$.

The loss-angle tangent for the mechanical problem, derived by analogy with the electrical case, is

$$\tan \theta = r\omega = \frac{\mu\omega}{E}. \tag{13}$$

It will be seen that by omitting the inertial term $qm\omega^2$ in equation (12) the phase-angle tangent and the loss-angle tangent *in the mechanical case* become identical.

In a non-inertial mechanical system such as that represented by the Voigt model alone, the loss-angle represents the amount by which the displacement would lag behind the impressed force on account of internal friction, represented by μ. As one goes from one material to another with increasing values of μ, but the same E, $\tan \theta$ and $\tan \phi$ increase for a given frequency. This implies an increase in the angle of lag. On the other hand, increases in the value of E reduce the loss angle; the elastic force tends to contribute toward overcoming the viscous resistance and bringing the displacement into phase with the impressed force.

Equation (13) indicates that the *relaxation time*, τ, originally applied to static experiments, is related to the angle of lag in a consistent manner. In materials having high relaxation times the displacement will lag farther behind the impressed force. (In the Voigt model, as in the simple capacitative-resistance circuit, no resonant condition can be attained, and, accordingly, in such a system a 90° lag of displacement behind force does not represent the most efficient operation.)

The angle of loss, as defined by equation (13), has been used by Kosten [6] and others to express results on rubber. The quantity $\mu\omega/E$, where μ and E referred to shear, has been called by Dillon, Prettyman, and Hall [5] the "molecular hysteresis defect." Nolle [9] has used the term "loss factor" for $\mu\omega/E$, although this is unfortunate, for "loss factor" and "loss-angle tangent" have different meanings in dielectric theory. In high polymers generally, μ is a function of ω in such a way that their product is nearly constant, and E is sensibly independent of frequency. Hence the quotient $\mu\omega/E$ represents a fairly reliable, frequency-independent index of the hysteretic losses in other high polymers as well as in textile materials.

In equation (4) the energy loss/cycle has been given as

$$H = Fs_m\pi.$$

This quantity represents the area of an ellipse having orthogonal half-axes F and s_m, for, in general, the area of an ellipse is given by $ab\pi$, where a and b are semi-axes. Such a figure would be described on the $F\cos\omega t - s$ plane only by a vibratory motion in which $F\cos\omega t$ is out of phase with s by 90°. This deduction is in conformity with the observation made above regarding the phase relations of $F\cos\omega t$ and s at resonance. Concerning the geometry of the dynamic stress-strain diagram, it can be concluded that the hysteresis loop is substantially an ellipse with major and minor axes lying on the $F\cos\omega t$ and s axes.

* In both the mechanical and electrical expressions given here for resonant frequency a term arising from dissipative effects, having a very small value, has been neglected.

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Announcement

COMMENCING WITH THE APRIL ISSUE, TEXTILE RESEARCH JOURNAL will expand its service to the industry by including papers which deal with subjects of interest to textile engineers and to others who are engaged in applied research. These reports are to appear in the JOURNAL in a section to be titled the "Industrial Section."

Articles will be reviewed by competent referees and will be accepted only if they meet a high editorial standard. Articles must be authoritative and they will be judged according to their usefulness and permanent reference value.

In the April issue the new section will include an important report titled "Crease-Resistance and Cotton." This report was prepared by George S. Buck, Jr., and Frank A. McCord, Technical Service Director and Market Research Director, respectively, of the National Cotton Council of America. This is a comprehensive study of the present status of crease-resistance, intended to assist those who may be interested in developing, through research, new crease-resistant treatments for cotton. Part I deals with potential markets. Part II, "Technical Aspects," which is the major portion of the paper, covers the following subjects: (1) Definitions; (2) Fiber Structure; (3) Fabric Construction; (4) Crease-Resistant Finishes; (5) Test Methods; (6) Topics for Research; and (7) Literature Sources, consisting of 165 references.

Papers on the following subjects will appear in early issues: a method for easier grade determination by measurement in wool top; a rapid stroboscopic method for the study of production looms; determination of inertia of rolls or cylinders; repeatability and tolerances of laboratory spinning techniques; and a study of the causes of end breakages in spinning.

An Experimental and Theoretical Study of the Adsorption and Swelling Isotherms of Human Hair in Water Vapor*

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Contribution of The Textile Foundation and of The Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Abstract

Quantitative data on the length and diameter changes accompanying the adsorption of water by human hair are given as functions of the relative humidity. Data are also given on the effects of a load on the swelling isotherms. A theoretical treatment is proposed which accounts in a semi-quantitative way for the swelling isotherms and the effects of tension as well as for the adsorption isotherm.

RECENTLY, several attempts have been made to interpret the water adsorption isotherms of organic fibrous materials quantitatively [5, 6, 7, 14, 29]. These differ widely in underlying physical assumptions and approximations involved in the derivation of the isotherm. However, each is reasonably successful in the fitting of experimental isotherms for a variety of substances. It is apparent, therefore, that the adsorption isotherm alone is not a sufficiently critical test of a theoretical approach.

Additional data available are, for the most part, heats and entropies of wetting. These are valuable but are closely related to, or often even derived from, the isotherm, and do not constitute enough supplementary evidence to determine the uniqueness of the proper physical assumptions.

Since swelling always accompanies the adsorption of water by the class of substances considered here, it is reasonable to observe swelling properties in an effort to obtain more information about the adsorption mechanism. The most direct way to do this is microscopically. This has been done before (see, for example, the work of Collins [9]) but always with common textile fibers, such as cotton or wool. There are disadvantages in the use of these fibers since their small diameters and irregular cross sections make them poor subjects for microscopic measurements. For this reason, most of the data taken on them is qualitative. However, it is often possible to find a large fiber of nearly circular cross section which is chemically very similar to a commercially important fiber. Such a fiber can be studied quantitatively with a microscope. The effects of tension on swelling are also interesting and important and readily lend themselves to study by microscopic techniques.

Data are presented here on the length and diameter changes of human hair, which is chemically similar to wool, under a small constant load and under no load. A theoretical treatment is given which, under certain conditions, is capable of interpreting the swelling isotherms and the influence of tension as well as the adsorption isotherm.

Experimental Procedure

In general, the experimental procedure used for swelling consisted of mounting a fiber in a small rectangular cell under tension supplied by a spring. The cell was humidified by a steady flow of air which passed through towers containing sulfuric acid of a known specific gravity. The length and diameter of the fiber were then measured as functions of the relative humidity and tension. The measurements were made with a microscope equipped with a micrometer eyepiece. Specifically, the experimental conditions were as follows:

Preparation of the Sample

The hairs were blonde human hairs, obtained through the courtesy of the Friez Instrument Divi-

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sion of the Bendix Aviation Company. They were extracted with alcohol and ether, washed in water, and air-dried after the method of Grundmann [13].

An effort was made to select samples with as round a cross section as possible. This was done by mounting fibers on a micromanipulator so that they could be turned through 360° and diameters measured frequently with the help of a microscope with a micrometer eyepiece. The hairs used were about 45 denier. The selected sample was then mounted in the conditioning cell.

Mounting

Hooks were fastened at both ends of the sample. Each hook consisted of two pieces of sheet phosphor bronze, one piece having a hook at one end. The two pieces were held together by a single screw (size 0–80) and it was found that, if the fiber was near the screw, no slipping at the hook occurred. The hooks weighed less than 0.1 gram each. After the hooks were fastened, the fiber was wetted in distilled water to remove any residual strains resulting from handling and then was mounted in the cell. Dry-length and -diameter measurements were obtained by passing air dried by passage through magnesium perchlorate over the fiber.

Cell and Microscope

The cell is shown in Figure 1, in a top view. The cell was used in a horizontal position except in the case of hair under no tension, as will be mentioned later. The sides (*a*) of the cell are brass or, in the case of an earlier cell, sealing wax. The top and bottom (*b*) are microscope slides. A hook (*c*) was mounted at one end opposite a hole (*k*) at the other. The fiber was mounted on hooks, one of which was linked to the fixed hook, the other to the spring (*d*). At approximately 3 cm. from the fixed hook a reference mark (*e*) was attached to the fiber. This was either a small piece of de Khotinsky cement or a small clamp of the same material as the end clamps. The spring was mounted on a movable collar (*f*) which can be adjusted by a screw (*g*) which runs through a fixed collar (*h*). Scratches (*i*) were made on the top microscope slide to give reference points for length measurements. The humidified air entered through a tube (*j*) and left at hole (*k*).

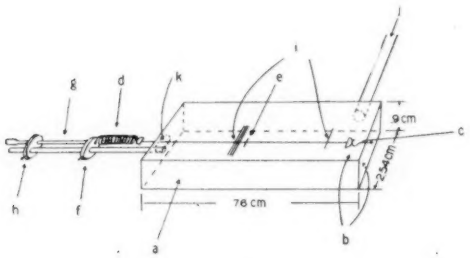

FIG. 1. *The adsorption cell.*

Humidity Control

The humidity was controlled by sweeping the cell with air passed through trains of sulfuric acid bottles, except at 100% relative humidity when water was used, and at 0% relative humidity when towers of concentrated sulfuric acid and magnesium perchlorate were used. Two bottles and a Milligan gas washing tower were used for each humidity. The rate of flow was about 300 cc./min.

The specific gravities of the sulfuric acid solutions were used in determining the relative humidities produced and were checked from time to time to assure constant relative humidity.

The air passing through the cell was proved to be at the desired humidity by an experiment in which it was passed through a tube of magnesium perchlorate and then through a flow meter. The tube was then weighed and the known amount of water in the known volume of air agreed with the theoretical value. Some extended experiments at low relative humidities proved back-diffusion of water vapor from the mouth of the cell to be no problem.

Temperature Control

The experiments were conducted at room temperature without thermostatting.

Tension Control

The tension on the fiber was controlled by means of calibrated springs. The springs were chosen so that any slight elongation of the fiber would produce a negligible change in the tension. The spring elongations were set visually against a steel scale. This system, unfortunately, did not give all the accuracy which might be desired. The error in the tensions is about ±0.2 g. The tensions were all chosen so as to minimize creep in the fiber during the course of the experiment.

Diameter and Length Measurements

Measurements were made with a 12.5 X micrometer eyepiece used with a 10 X objective. The

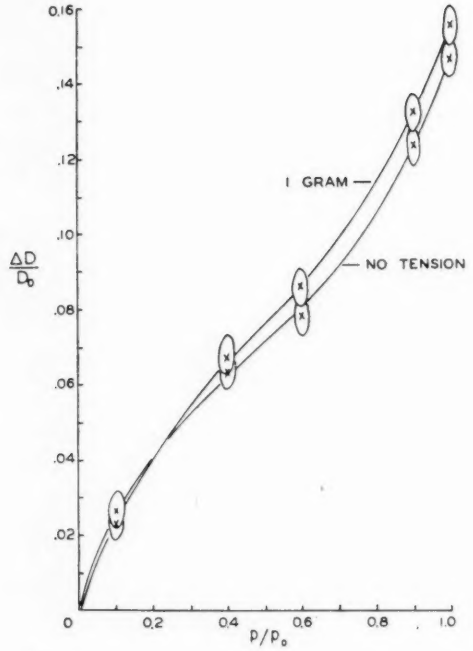

FIG. 2. *The change in diameter with change in relative humidity of human hair under no tension and 1 gram tension.*

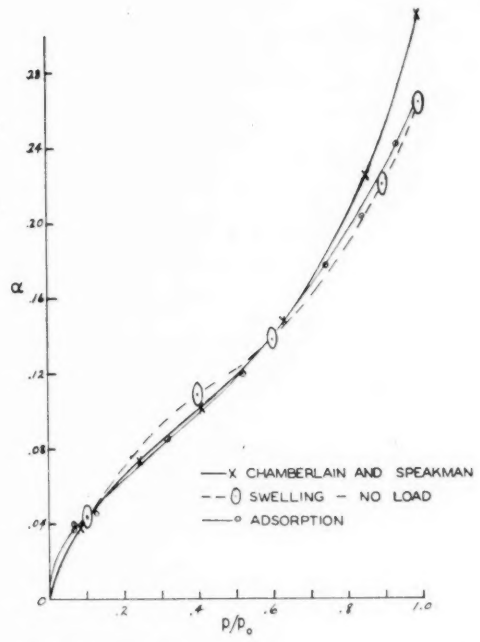

FIG. 4. *Comparison of a plot of regain versus relative humidity taken from swelling data with experimental adsorption isotherms.*

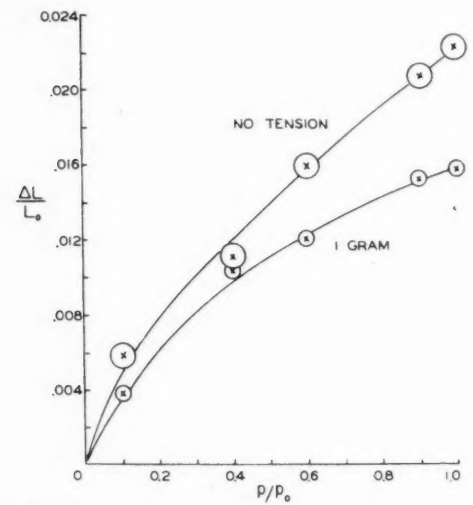

FIG. 3. *The change in length with change in relative humidity of human hair under no tension and 1 gram tension.*

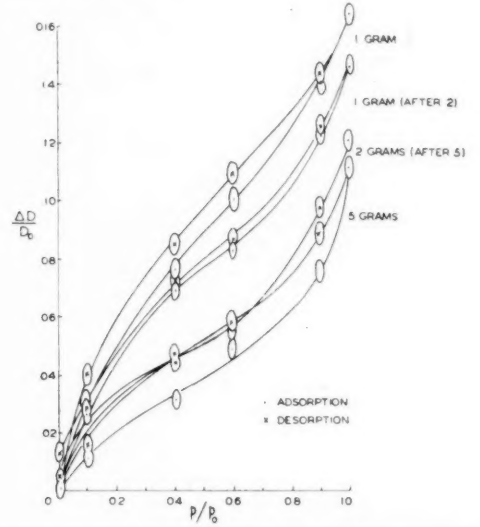

FIG. 5. *Changes in diameter with changes in relative humidity of human hair under various tensions.*

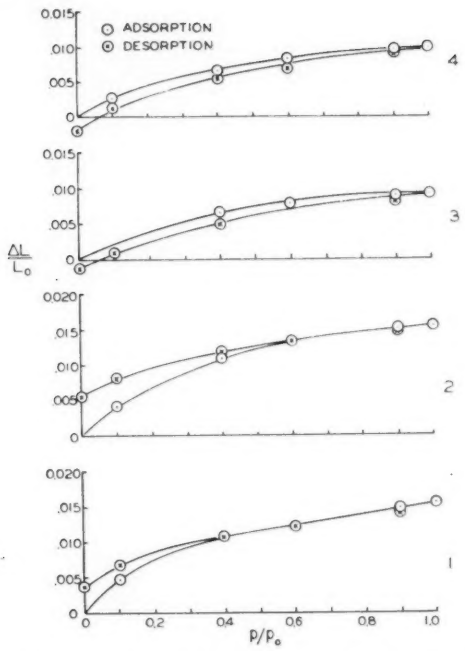

FIG. 6. *Changes in length with changes in relative humidity of human hair under various tensions: (1) 1 gram tension, (2) 5 grams tension after 1 gram, (3) 2 grams tension after 5 grams, (4) 1 gram tension after 2 grams.*

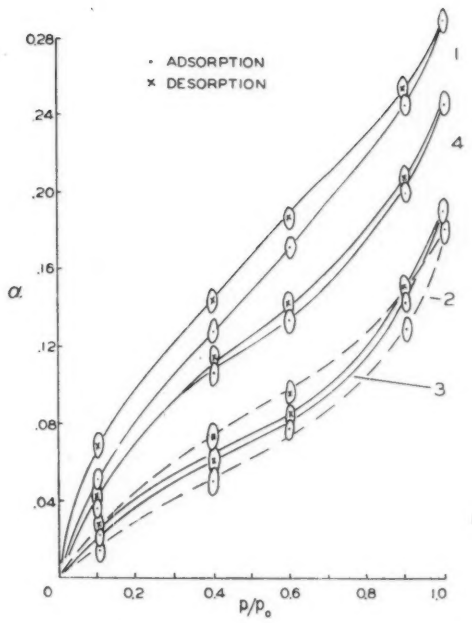

FIG. 7. *Adsorption isotherms derived from swelling data for human hair under various tensions: (1) 1 gram tension, (2) 5 grams tension, (3) 2 grams tension after 5 grams, (4) 1 gram tension after 2 grams.*

fiber diameter was measured at 20 approximately equally spaced positions. Two complete sets of 20 diameter readings were taken for each determination in order to render it unlikely that serious observational or recording error had been made at any individual position. It is essential that the individual fiber diameters be read at the same twenty points for each series of measurements. Two com-

TABLE I

	Tension = 0 grams			Tension = 1 gram		
R. H.	$\frac{\Delta D^*}{D_o}$	$\frac{\Delta L}{L_o}$	α	$\frac{\Delta D}{D_o}$	$\frac{\Delta L}{L_o}$	α
10	.0261	.0058	.044	.024	.0038	.039
40	.064	.0111	.109	.067	.0103	.112
60	.078	.0159	.1375	.086	.0120	.143
90	.124	.0206	.221	.133	.0152	.222
100	.147	.0222	.264	.156	.0157	.268

* D = diameter. L = length.

TABLE II

	Tension = 1 gram			Tension = 5 grams			Tension = 2 grams			Tension = 1 gram		
R. H.	$\frac{\Delta D}{D_o}$	$\frac{\Delta L}{L_o}$	α	$\frac{\Delta D}{D_o}$	$\frac{\Delta L}{L_o}$	α	$\frac{\Delta D}{D_o}$	$\frac{\Delta L}{L_o}$	α	$\frac{\Delta D}{D_o}$	$\frac{\Delta L}{L_o}$	α
10	.0291	.0047	.0505	.013	.0042	.0162				.030	.0026	.0375
40	.075	.0107	.128	.031	.0108	.0514	.045	.0065	.0633	.069	.0066	.1085
60	.101	.0121	.172	.049	.0131	.0846	.055	.0077	.0800	.083	.0082	.1331
90	.142	.0145	.247	.076	.0152	.129	.095	.0088	.1457	.123	.0094	.204
100	.164	.0154	.289	.111	.0154	.186	.120	.0091	.190	.147	.0097	.245
90	.144	.0141	.246	.088	.0146	.147	.097	.0081	.150	.125	.0090	.207
60	.109	.0121	.192	.058	.0133	.0978				.087	.0068	.1414
40	.084	.0106	.144	.045	.0116	.0782	.0436	.0049	.0574	.071	.0053	.1132
10	.040	.0067	.068	.015	.0081	.0242	.026	.0009	.0286	.030	.0013	.0413
0	.003	.0035	.008	.000	.0057	.002	.005	−.0011	.000	.012	−.0015	.0138

plications appeared in attempting to measure the diameter of fibers. The fibers had an irregular cross section, usually approaching an ellipse. Also, as the conditions of tension and humidity were changed there was rotation of the fiber. The cross section of hair was not uniform along the fiber but, at any angle of observation, a representative number of major, minor, and intermediate axes presented themselves. Thus, rotation caused no change in the average diameter determined. Length measurements were made by focusing first on the hooks holding the fiber and then on the reference marks on the cover glass. The eyepiece allowed reproducible readings to within ±0.0001 cm.

By applying statistical methods [25] it is possible to obtain a value for the standard deviation of the mean of the 20 diameter measurements. The standard deviation of the length measurements cannot be determined statistically but an upper limit can be set for this error. The following formula for combining errors is used to determine the error of the square of the diameter which is then used to obtain the error of the volume:

$$(D \pm d)^2 = D^2 \left\{ 1 \pm \frac{2d}{D} \right\},$$

where D is the average diameter and d is its corresponding error. This formula is suitable as long as d/D is not very large. A more accurate method would involve the use of logarithms to combine the errors. The two methods give identical results here. It was found that the error in length measurements made a negligible contribution to the error of the volume.

A typical value obtained for the standard deviation of the volume for hair was 0.5%. This value was subject to considerable variation, depending upon the roundness of the hair chosen.

The symbols used to denote experimental points in the graphs of this paper are drawn to a scale indicating twice the standard deviation in the case of diameter and length measurements. This indicates the significance of the separation of various points.

Attainment of Equilibrium

Rate curves indicated that equilibrium was usually reached in 4 hours. No experimental points are given, however, which were taken in less than 8 hours. It is worth pointing out the difference between the rates for single fibers and for bulk samples which are notoriously slow in reaching equilibrium. Apparently, the diffusion into the bulk sample is slow, quite apart from diffusion into the fiber proper.

Experiments Under No Tension

Data are also given for fibers under no tension. These are taken in the same way as for the tensioned fibers except that only one end of a short (1.5-cm.) sample is clamped and the cell is mounted vertically instead of horizontally.

Experimental Results

The experimental results are summarized in Figures 2–7 and Tables I–II. Three types of data are given: diametral swelling isotherms, longitudinal swelling isotherms, and adsorption isotherms derived from swelling isotherms. The adsorption isotherms are derived on the assumption that each water molecule contributes its usual molecular volume to swelling the fiber. As such, the amount adsorbed is equal to the product of the ratio of the volume change to the initial dry volume and the ratio of the densities of water and of the dry fibers. The value of the density used for hair was 1.32, which is the value for wool [16]. This gives α, the amount adsorbed, or regain, in grams of water per gram of dry fiber.

Figures 2–4 and Table I give data for hair under no load and under 1-gram load. The samples are consecutive sections of the same hair.

Figures 5–7 and Table II give results for a single sample under successive loads of 1, 5, 2, and 1 g.

There are several interesting features of these data:

1. All of the curves show large changes at low relative humidities, indicating that swelling is important from the start of the adsorption process. Condensation or adsorption on extensive internal surfaces without swelling is not present.

2. The large changes of the curves for the diametral change and the regains at high relative humidities (remembering that the regain used here is directly related to the volume change) indicate there is no extensive system of permanent capillaries since condensation into permanent capillaries would be accomplished without swelling. Furthermore, the calculations of Barkas [2] make it unlikely that collapsing capillaries of any considerable size exist in substances having moduli of rigidity of the order of magnitude of that probable for hair. In con-

nection with capillaries, it should be mentioned that hairs with lumina were not used.

3. In Figure 4 the adsorption isotherm derived from swelling measurements on a hair under no tension is compared with one given by Chamberlain and Speakman [8] and with original data.* The original adsorption data and swelling data were taken on different portions of the same sample. Both of the adsorption isotherms were obtained by conventional weighing methods.

The assumption that every adsorbed molecule contributes to the swelling seems justifiable to a good approximation for hair. The true microscopic density of a fiber is, strictly speaking, undefinable, or at least very difficult to measure [17], so that the use of 1.32 for the density of hair might be questioned, as might the use of the bulk density of water. However, small changes in these values would alter the end result only slightly.

The derived regain isotherm lies below the experimental ones at the highest relative humidities. The differences between the two curves for the same hair are practically negligible. These small differences are probably attributable to differences in experimental technique. The difficulties of maintaining high humidities without condensation, especially with bulk samples, are well known. In addition, as has been pointed out by Urquhart and Williams [27], the bulk sample supplies a system of small capillaries capable of taking up water at pressures below saturation.

However, one further fact must be mentioned. The data presented compare the properties of an individual hair with data on a bulk sample. Some other hairs have shown a lower derived regain isotherm. Since non-additivity of volumes is the rule rather than the exception with fibrous materials it seems probable that a small indeterminate error is being introduced here.

4. A comparison of the isotherms for the change in diameter with those for the change in length (see Figures 2 and 3) shows that they not only differ in magnitude but also in shape. This suggests that the anisotropic effects are more than just a matter of degree and indicate a fundamental difference in mechanism.

5. Application of tension to the fiber decreases the swelling and hence the amount adsorbed at a given relative humidity.† The effects of an increase in tension are particularly evident in the diametral changes.

6. Finally, it is evident that hysteretic effects occur, as is usual with this type of material. The hysteresis can be seen in the difference between the adsorption and desorption curves. Also, the difference between the isotherms for hair with 1-gram load before and after a 5-gram load is a form of hysteresis.

Discussion of Previous Theories

The foundation for the quantitative interpretation of sigmoid adsorption isotherms lies in the multilayer adsorption picture of Brunauer, Emmett, and Teller [4]. The Brunauer-Emmett-Teller isotherm was originally derived by a detailed consideration of the rates of condensation and evaporation in a multilayer system on a surface. The surface was assumed to be capable of being covered by a strongly bonded layer. On top of molecules bound on strongly bonding sites, molecules could condense to form multilayers. These weakly bound molecules were assumed to be in a state thermodynamically similar to that in liquid water.

Many variants of this concept exist but all are based on the same fundamental picture—there exist simultaneously sites of strong and weak bonding on the adsorbent. The variations are concerned with the dependence of the number of weak bonding sites upon the number of strong bonding sites, with how the configurational entropy from the weak bonding sites should be determined, and with the heat and entropy of bonding on the weak bonding sites. References [5, 6, 7, 14] are concerned with variations designed specifically to apply to fibrous materials. Two additional papers should be mentioned: Dole [10] and Barrer [3] propose treatments but do not apply them.

The specific set of equations derived by Brunauer, Emmett, and Teller have been of great utility because of their simplicity of form. However, two major objections prevent their direct use for fibrous materials: First, the equations were originally derived for adsorption on a surface only, whereas adsorption of water occurs throughout the bulk of

* We are indebted to Mr. I. Amron and Mr. W. Barnard, who obtained these data.

† This assumes that the fiber-water system is incompressible. Rough experiments measuring regain under tension directly have been made while this paper was in press. These indicate a possible compression under tension. Further work is needed to resolve this point.

fibrous materials. Secondly, the equations were derived postulating no change of the physical state of the adsorbent.

It is possible, of course, to postulate a large, internal surface in fibers. However, experimental evidence, some of which has been given earlier in this paper, is against the existence of such a surface which in the conventional sense is a discrete interface between a solid and a bulk liquid or gaseous phase. Perhaps the most direct evidence against an internal surface is that of Rowen and Blaine [24], who showed that adsorption isotherms for N_2 at liquid-air temperatures led to surface areas of the same order of magnitude as given by microscopic estimates based on the external surface.

The work of Hill [19] and Cassie [7] has furnished the solution of the first problem since they have shown, by deriving the multilayer adsorption equations by statistical mechanical methods, that the form of the equations is not changed on generalizing from sites of strong bonding in two dimensions to sites of strong bonding in three dimensions if the other assumptions are kept.

The differences between the theories mentioned lie primarily in the methods of treating the second problem—the physical changes of the adsorbent—or in varying the heats and entropies of the weakly bonded molecules, which is an allied problem.

The theoretical treatments may be divided into three groups according to the mode of approach: (1) Dole, (2) Cassie, and White and Eyring, (3) Hailwood and Horrobin, and Barrer.

Dole has used the formal approach of Hill [19] (see also Hill [20]) to develop more general isotherms based on the Brunauer, Emmett, and Teller (B.E.T.) picture. The same dependence of number of weak bonding sites on number of strong bonding sites and the same configurational entropy are used. However, the generalizations provide for the heat of adsorption of the weakly bonded molecules varying according to the distance from the strong bonding site and for some interaction between adjacent molecules in the same layer. Dole states that he specifically considers a system in which the physical state of the adsorbent does not change. However, a heat or entropy change caused by the swelling of the structure of the adsorbent will be reflected by a corresponding change in the total heat or entropy of adsorption. Thus, the changes necessary to make a hole for a molecule would cause changes in the free energy of adsorption of that molecule. To this extent at least, Dole's equations can be applied to swelling adsorbents. However, mathematical complexities limit to various simple progressions the relationships between the heats of adsorption in successive layers, which can be solved to give a usable isotherm. The fundamental physical postulates underlying these progressions are obscured and the use of an isotherm so derived, in other than an empirical way, is impaired.

The theories of Cassie [5, 6] and White and Eyring [29] both attempt to account for the changes of the adsorbent directly.

Cassie attempts to calculate the free energy changes assumed to be purely heat changes, caused by the extension of the adsorbent, making use of the work of Barkas [1, 2] and Warburton [28]. Barkas and Warburton make use of the classical theory of elasticity to calculate the energy and pressure changes within an anisotropic elastic cylinder caused by deformation in terms of the moduli, Poisson's ratios, and thermal coefficients of the cylinder. This assumes that swelling by water and the sum of the various corresponding external deformations require the same energy change. The heat (or pressure) term thus deduced is then used to correct the free energy (or pressure) of the experimental isotherm and give the so-called "stress-free" isotherm, which is then treated by the simple B.E.T. equation.

This treatment of the swelling term is exact in so far as the swelling substance can be treated as an elastic body. However, the equations developed for the swelling term are differential equations applicable to infinitesimal swelling changes of the system considered. Hence, strictly speaking, the moduli, etc., should be determined for small differences of regain and the energy of swelling for a finite change obtained by graphical integration. Thus, a great amount of data is needed to evaluate successfully all of the moduli, etc., needed to calculate the swelling term. Actually, assumptions and approximations as to the nature of the swelling network must be made, also, to derive a working swelling equation.

White and Eyring attempted to evaluate the swelling free energy of the adsorbent in terms of the partition function of a simplified network assumed to have the same over-all mechanical properties as the adsorbent. The free energy equation for the B.E.T. theory was then modified by the introduction of this term. The success of this method ob-

viously depends upon, among other things, the correspondence of the assumed network with the actual adsorbent structure. The networks discussed by White and Eyring were the isotropic network of entropy springs familiar in the case of rubber and a network of rods held together by springs and capable of two-dimensional isotropic swelling. These are undoubtedly poor approximations to an actual fiber, and the assumption and evaluation of an entirely satisfactory network are difficult and, at present, unsolved problems. However, there appear to be certain merits to this approach. First, it is a probability, strengthened by the partial success of the kinetic theory of rubber, that the mechanical properties of complex substances can be expressed in terms of relatively few molecular constants and that the influences on these properties of substances such as water can be evaluated in terms of the reactions involved. Second, because of its unity and simplicity, the partition function approach, specifically including the adsorbent proper, offers perhaps more versatility for testing various possible physical assumptions than does Dole's approach.

In this connection, it may be well to emphasize the connection between the two approaches in so far as swelling is concerned. Dole considers the addition of each water molecule to a system composed of the adsorbent and all previously adsorbed water molecules. Cassie and White and Eyring consider the expansion of the adsorbent to its final dimensions and the subsequent addition of water without swelling. The two methods merely approach the change of state by alternate paths and hence are undistinguishable from the standpoint of free energy change involved except for utility of calculation.

The final mode of approach is that of Hailwood and Horrobin [14] and Barrer [3]. These authors consider the strong and weak types of adsorption to be independent. The strong adsorption is considered to occur with a large heat change on a definite number of sites. The weak adsorption is considered to occur simultaneously and independently and to be caused by an increase in entropy resulting from the mixing of water molecules and segments of adsorbent molecules. Hailwood and Horrobin use Henry's law to express the solubility of water in the adsorbent for the weakly bonded molecules. This approach implies an ideal mixing which is not to be expected in the polymeric systems which are dealt with here. For this reason their treatment is open to criticism. As Barrer points out, treatments accounting for deviations from ideal mixing when heat effects are not too important are known and have been applied to the swelling of rubbers by non-polar liquids [12]. Barrer suggests the same picture as do Hailwood and Horrobin except that this treatment be used for the mixing term.

The importance of such a mixing term will vary with the individual case. In general, it becomes more important as the adsorbents become more rubberlike and the adsorbates less polar. An analysis of the swelling data in this paper argues against its being important in the case considered quantitatively here except possibly at very large regains (see also the work of Cassie [6]). However, additional information, possibly from the analysis of the influence of temperature on adsorption, is needed to decide the magnitude of the possible mixing term.

Theory Used in This Paper

The data on swelling which have already been presented in this paper, coupled with earlier data on adsorption and fiber structure in general, place several limitations on possible mechanisms for adsorption. A mechanism is presented here which is in qualitative agreement with the facts as they are known. In addition, a theoretical treatment, similar to that of White and Eyring, is derived and applied to some of the data for hair.

Three facts are evident from the swelling data on hair: (1) to a good approximation, every water molecule adsorbed swells the adsorbent; (2) the length and diameter swelling isotherms differ in shape and degree; (3) application of tension reduces the amount of swelling and, hence, the amount adsorbed at a given relative humidity.

A variety of experimental facts has given the following rough picture of a keratin fiber. The fiber consists of long molecular chains (polypeptide chains) the long axes of which roughly parallel the fiber axis. The fibers are radially symmetrical and are held together laterally by some primary cross-links and by hydrogen bonds (between amide linkages on neighboring chains) and van der Waals forces. This description is enough to indicate a mechanism for the difference between the length and diameter swelling isotherms. It has been shown that most of the water adsorbed contributes to the swelling. This means that an entering water molecule must force its way between segments of

the fiber network structure. If the chains of the network are oriented along the axis of the fiber, this means that swelling will occur in the diametral direction only. However, it is known from thermodynamic data that a certain fraction of the water adsorbed is strongly bound on sites within the fiber. If it is assumed that this strong bonding corresponds to a hydration of segments or residues of the network chains, then the length swelling can be understood. It is not unreasonable to expect that the dimensions of a segment or residue change on hydration so that adsorption on strong bonding sites alters both radius and length. Thus the change in length depends upon the number of water molecules adsorbed on strong bonding sites, while the change in diameter depends on the total number adsorbed. Since the number adsorbed on the strong bonding sites roughly follows a Langmuir adsorption isotherm and asymptotically approaches a maximum, the length change will also follow such an isotherm while the diameter change isotherm will have the customary sigmoid shape, since the weakly adsorbed molecules will influence the diameter but not the length. It should be stressed that in this case every residue or segment in a chain increases in length when it is hydrated, causing an over-all increase in length of the chain composed of these residues.

The influence of tension can also be understood in terms of this model. It has already been mentioned that the tensions used in these experiments were so small that mechanical creep was unimportant. Since hydration increases the length of the segment hydrated, application of a tension would tend to decrease the amount of hydration at a given relative humidity—by Le Chatelier's principle, whereby a system at equilibrium changes to counteract the influence of an external stress. Since the number of sites for weak bonding is dependent upon the number of strongly bonded molecules, if the B.E.T. picture is used, an increase in tension will also decrease the lateral swelling.

Another possible reason for swelling anisotropy could be put forward as follows: Consider a fiber composed of long, thin micelles capable of adsorbing water on their surfaces. Such a fiber would show anisotropy of swelling because of the unequal distribution of available surface per unit length in the radial and axial directions. However, in this case, the length and diameter swelling isotherms would differ only in amount and not in shape. Furthermore, application of a tension would have no influence on the strongly bound water molecules on the sides of the micelles and, hence, none on the lateral swelling. Therefore, such a mechanism is inconsistent with the observed data.

One further fact can be obtained from a consideration of the shapes of the diameter and length swelling isotherms. A large free mixing term would be associated with a decrease in anisotropy in the swollen gel which would probably be reflected by a contraction in length as the volume increased, in the case of hair. This does not happen and, hence, a large free mixing term is unlikely. However, it is probable from permeability experiments on films that complete omission of such a term is an oversimplification.

A quantitative treatment will next be given based on the following physical assumptions: The fiber will be considered to be formed by long chains of rigid molecules oriented parallel to the axis of the fiber. The degree of rigidity is not important as long as free mixing does not contribute appreciably to the swelling. The fiber is isotropic radially and held together by occasional primary cross-links and by hydrogen bonds. The cross-bonds, both primary and secondary, will be assumed to act either radially or tangentially but always in a direction perpendicular to the fiber axis. The primary cross-bonds are infrequent enough so that the molecular chains react to small axial stresses independently, as far as equilibrium properties are concerned. This assumption is also often made implicitly in discussions of mechanical properties.

Two types of adsorption can occur—adsorption on fixed strongly bonding sites and adsorption on weakly bonding sites where the adsorbed molecule is in a state thermodynamically similar to the liquid state. The number of weakly bonding sites is determined by the number of strongly bonding sites. The strong bonding corresponds to hydrate formation and may change the dimensions and mechanical properties of the residue hydrated. The weak bonding causes separation of adsorbent chains but does not change their properties. Every molecule adsorbed swells the adsorbent network.

The partition function for a strongly bonded water molecule may be written:

$$\left(\frac{kT}{h\nu_s}\right)^3 j_s' e^{\epsilon'/kT} = j_s e^{\epsilon/kT}, \qquad (1)$$

where k is the gas constant per molecule; T, the absolute temperature; h, Planck's constant; ν_s, the

average characteristic vibrational frequency of a strongly adsorbed molecule; j_s^i, the internal degrees of freedom of a strongly adsorbed molecule; and $-\epsilon$, the energy of adsorption.

The partition function for a weakly bonded water molecule may be written:

$$\left(\frac{kT}{h\nu_L}\right)^3 j_L{}^i e^{\epsilon_{vap}/kT} = j_L e^{\epsilon_{vap}/kT}, \tag{2}$$

where ν_L is the average characteristic vibrational frequency in the liquid state; j_L^i, the internal degrees of freedom in the liquid state; and $-\epsilon_{vap}$, the energy of vaporization. Since these partition functions enter only in a constant term in the final equations, other forms for each partition function will affect independent evaluation of the constant but not the shape of the isotherm. Since the constants are evaluated from experimental data here, the forms of the partition functions used are sufficient for the purposes at hand.

It is now necessary to consider the effects of the tension on the fiber. The fiber has been assumed to be composed of a number of molecular chains which act independently as far as small axial stresses are concerned. The tensions used have been chosen so that creep effects are unimportant and the fiber acts as a spring, or

$$f = \psi l, \tag{3}$$

where f is the force per unit area; ψ, the elastic constant; and l, the strain. If each chain can be given a cross-sectional area, Γ, then

$$f\Gamma = \psi l\Gamma$$

is the force per chain, or $\frac{\psi l^2\Gamma}{2}$ is the potential energy per unit length of the molecular chain. If λ is the length of one of the residues of which the chain is composed,

$$\frac{\psi l^2\Gamma\lambda}{2} = \frac{\psi l^2\omega}{2}$$

(where ω is the volume of a residue) is the potential energy per residue.

Since hydrated and unhydrated residues are assumed to have different physical properties, the partition function for an unhydrated residue can be written

$$e^{-\frac{l^2\omega_1}{2\psi_1 kT}}, \tag{4}$$

and that for a hydrated residue as

$$e^{-\frac{l^2\omega_2}{2\psi_2 kT}}, \tag{5}$$

where the subscripts refer to the state of hydration.

Let α be defined as the total number of water molecules adsorbed per gram of fiber at a relative humidity, p/p_o; B, as the total number of sites for strong bonding, or hydration, per gram of fiber; and x, as the number of the α molecules adsorbed which are adsorbed on strong bonding sites. Then, the partition function for all the strongly bonded molecules is

$$Q_1 = \frac{B!}{x!(B-x)!}(j_s e^{\epsilon/kT})^x. \tag{6}$$

The partition function for the $(\alpha - x)$ weakly bonded molecules can be written

$$Q_2 = \frac{(\alpha-1)!}{(x-1)!(\alpha-x)!}(j_L e^{\epsilon_L/kT})^{\alpha-x}. \tag{7}$$

The first term of equation (7) represents the number of ways $(\alpha - x)$ beads may be strung on x strings with no limitations on the number per string. The partition function for all unhydrated residues can be given by

$$Q_3 = (e^{-\frac{l^2\omega_1}{2\psi_1 kT}})^{A-x}, \tag{8}$$

where A is the number of residues per gram of fiber. In a physically and chemically homogeneous fiber where there is one strong bonding site per residue, $A = B$. In other fibers, ω_1 and ψ_1 are average values and A may not equal B. Similarly, the partition function for the hydrated residues may be written

$$Q_4 = (e^{-\frac{l^2\omega_2}{2\psi_2 kT}})^x. \tag{9}$$

Finally, the partition function for the change in physical state of the network occurring as a result of swelling may be indicated by Q_5. This need not be specified further at the moment, other than to state that it depends upon α only. Combining terms, the total partition function is

$$\begin{aligned} Q &= \sum_{x=1}^{K} (Q_1Q_2Q_3Q_4Q_5) \\ K &= \alpha,\ \alpha \le B \\ K &= B,\ \alpha > B \end{aligned} \tag{10}$$

The value of $\log Q$ is now desired. This may be determined by setting $\log Q$ equal to the log of the largest term in the sum, to a good approximation, in this case. This term may be found by using

$$\frac{\partial \log Q}{\partial x} = 0, \tag{11}$$

which gives

$$(B - x)(\alpha - x) = \beta x^2, \tag{12}$$

where

$$\beta = \frac{j_L}{j_s} e^{\frac{\epsilon_L - \epsilon}{kT}} e^{\left(\frac{f^2 a_2}{2 s_o^2 kT} - \frac{f^2 a_1}{2 r_o^2 kT}\right)}$$

is the value of x at a given value of α. The partial molal free energy of the adsorbate, μ_1, can be evaluated from the expression

$$\frac{\mu_1}{kT} = -\frac{\partial \log Q}{\partial \alpha} = -\log \alpha + \log (\alpha - x) - \log (j_L e^{\epsilon_L / kT}) + \frac{\mu_{1N}}{kT} \tag{13}$$

if the value of μ_{1N}, the partial molal free energy contribution from the swelling of the network, can be evaluated.

For the vapor,

$$\frac{\mu_1}{kT} = \frac{\mu_{10}}{kT} + \log p, \tag{14}$$

where μ_{10} is a constant of the temperature and atmosphere pressure and p is the vapor pressure. For the liquid in equilibrium with the saturated vapor,

$$\frac{\mu_1}{kT} = -\log (j_L e^{\epsilon_L / kT}) = \frac{\mu_{10}}{kT} + \log p_o, \tag{15}$$

where p_o is the vapor pressure over the liquid. By combining equations (13), (14), and (15), the second part of the isotherm can be written

$$\log \frac{\alpha - x}{\alpha} + \frac{\mu_{1N}}{kT} = \log p / p_o. \tag{16}$$

α, x, and B can now be expressed as grams of water per gram of fiber, for convenience.

It is now necessary to consider the evaluation of μ_{1N}. As has already been stated, the physical model to be used for a fiber consists of long rigid molecules held together by primary cross-bonds and secondary hydrogen bonds. The cross-bonds may be either radial or tangential but are always perpendicular to the long axis of the molecule and hence of the fiber. The fiber will be assumed to act as a unit with all micro-deformations equal to macro-deformations. Swelling deformations will be considered to be entirely radial to a first approximation.

Consider one gram of the dry fiber. Let there be N_1 cross-bonds parallel to a radius, N_2 cross-bonds perpendicular to a radius, N_3 hydrogen bonds parallel to a radius, and N_4 hydrogen bonds perpendicular to a radius.

Let the potential energy for one of the N_1 bonds be given by

$$V_1 = \frac{\phi_1}{2 r_o} (r - r_o)^2, \tag{17}$$

where ϕ_1 is the spring constant for the cross-bonds and r_o is its equilibrium unstressed length.

The potential energy for one of the N_2 bonds can then be written

$$V_2 = \frac{\phi_2}{2 s_o} (s - s_o)^2, \tag{18}$$

where ϕ_2 and s_o have meanings analogous to those for the N_1 molecules.

Let the potential energy for one of the N_3 bonds be given by

$$V_3 = -\frac{\epsilon_1 \epsilon_2}{z} + \frac{\epsilon_2 \epsilon_3}{z'}, \tag{19}$$

where ϵ_1, ϵ_2, and ϵ_3 are effective charges on the hydrogen, the atom to which it is hydrogen-bonded, and the atom to which it is chemically bonded, respectively. z and z' are the separations of the charges.

The potential energy for the N_4 bonds can then be given as

$$V_4 = -\frac{\epsilon_1 \epsilon_2}{y} + \frac{\epsilon_2 \epsilon_3}{y'}, \tag{20}$$

where the ϵ's and y's have meanings analogous to those above for ϵ's and z's.

Since swelling is assumed to be uniform, r can be related to D, the fiber diameter, by some proportionality factor, $1/c_1$. Since the circumference of a circle is simply related to the diameter, s can be related to D by $1/c_2$. The constants r_o and s_o can be written as $\frac{d_o}{c_1}$ and $\frac{f_o}{c_2}$, respectively. x and x' can be set equal to r minus constant values $\frac{g_1}{c_1}$ and $\frac{g_2}{c_1}$, respectively, and y and y' to s by $\frac{g_3}{c_2}$ and $\frac{g_4}{c_2}$, respectively.

The total potential energy for the gram of fiber can be written (in terms of the fiber diameter, D)

$$V = \frac{N_1 \phi_1}{2 d_o c_1} (D - d_o)^2 + \frac{N_2 \phi_2}{2 f_o c_2} (D - f_o)^2 - \frac{N_3 \epsilon_1 \epsilon_2 c_1}{D - g_1} + \frac{N_3 \epsilon_2 \epsilon_3 c_1}{D - g_2} - \frac{N_4 \epsilon_1 \epsilon_2 c_2}{D - g_3} - \frac{N_4 \epsilon_2 \epsilon_3 c_2}{D - g_4}. \tag{21}$$

The partial molal free energy change for the water can then be written (mixing terms are neglected as has been discussed)

$$\mu_1 = \frac{\partial \Delta A}{\partial \alpha} = \frac{\partial (V - V_o)}{\partial \alpha} = \frac{\partial V}{\partial D}\frac{\partial D}{\partial \alpha}. \qquad (22)$$

Since the swelling is considered to be entirely radial (the error introduced by ignoring the length change is small ($\sim 1\%$) because of the relative magnitudes of the length and diameter changes),

$$\frac{\pi D^2 L_o}{4} = V_o + \alpha v = V_o + \alpha, \qquad (23)$$

where L_o is the length of one gram of fiber; V_o, the dry volume per gram of the fiber; and v, the volume added per unit of water which is equal to unity if α is expressed in grams.

$$D = \left[\frac{4}{\pi L_o}(V_o + \alpha)\right]^{\frac{1}{2}} = D_o\left(\frac{V_o + \alpha}{V_o}\right)^{\frac{1}{2}} = D_o v_2^{-\frac{1}{2}}, \qquad (24)$$

where v_2 is the volume fraction of polymer present in the polymer-water system. Now,

$$\frac{\partial D}{\partial \alpha} = \frac{1}{2}\frac{D_o}{V_o} v_2^{\frac{1}{2}}. \qquad (25)$$

Combining equations (22)–(25):

$$\mu_1 = \frac{1}{2}\frac{N_1\phi_1 D_o^2}{d_o V_o c_1} - \frac{N_1\phi_1 D_o d_o}{2 d_o c_1 V_o} v_2^{\frac{1}{2}} + \frac{N_2\phi_2 D_o^2}{2 f_o V_o c_1} - \frac{N_2\phi_2 D_o f_o}{2 f_o V_o c_1} v_2^{\frac{1}{2}} + \frac{D_o N_3 \epsilon_1 \epsilon_2 c_1}{2 V_o\left(\frac{D_o}{v_2^{\frac{1}{2}}} - g_1\right)^2} v_2^{\frac{1}{2}} - \frac{D_o N_3 \epsilon_2 \epsilon_3 c_1}{2 V_o\left(\frac{D_o}{v_2^{\frac{1}{2}}} - g_2\right)^2} v_2^{\frac{1}{2}} + \frac{D_o N_4 \epsilon_1 \epsilon_2 c_2}{2 V_o\left(\frac{D_o}{v_2^{\frac{1}{2}}} - g_3\right)^2} - \frac{D_o N_4 \epsilon_1 \epsilon_2 c_2}{2 V_o\left(\frac{D_o}{v_2^{\frac{1}{2}}} - g_4\right)^2}. \qquad (26)$$

This formula is too complicated to use; however, if it is assumed that $g_1, g_2, g_3, g_4 \ll \frac{D_o}{v_2^{\frac{1}{2}}}$ and $d_o \cong f_o \cong D_o$, and $\phi_1 = \phi_2$, the expression is reduced to

$$\frac{\mu_{1N}}{kT} = \gamma(1 - v_2^{\frac{1}{2}}) + \eta v_2^{\frac{1}{2}}, \qquad (27)$$

where

$$\gamma = \frac{1}{kT}\left(\frac{N_1}{c_1} + \frac{N_2}{c_2}\right)\left(\frac{1}{2}\frac{\phi D_o}{V_o}\right)$$

and

$$\eta = \frac{N_3\epsilon_2 c_1(\epsilon_1 - \epsilon_3)}{2 V_o D_o kT} + \frac{N_4\epsilon_2 c_2(\epsilon_1 - \epsilon_3)}{2 V_o D_o kT}.$$

The assumptions with respect to the g's, d_o, and f_o are probably satisfactory except in the case of g_1 and g_3 where a rough estimate of as high as 25% error can be made. The error possible in this approximation tends to emphasize the importance of the swelling term.

Equation (27) can now be substituted in (16), which, combined with (12), gives the isotherm.

$$(B - x)(\alpha - x) = \beta x^2;$$

$$\log\left(\frac{\alpha - x}{\alpha}\right) + \gamma(1 - v_2^{\frac{1}{2}}) + \eta v_2^{\frac{1}{2}} = \log\frac{p}{p_o}. \qquad (28)$$

Consideration of the relative magnitudes of the two swelling free-energy terms shows that γ must be about ten times larger than η in order for the first term to exert an appreciable effect on the adsorption. Since this is often unlikely in the case of fibers because of the small or even nonexistent number of primary cross-bonds, the first term probably may be omitted in many cases.

The elongation of the fiber at a given relative humidity and tension can now be given as

$$l = \frac{A - x}{A}\frac{1}{\psi_1} f + \frac{x}{A} l_{12} + \frac{x}{A}\frac{1}{\psi_2} f, \qquad (29)$$

where A is the number of residues per gram of fiber and may or may not be equal to B, depending upon the chemical and physical composition of the fiber. l_{12} is the elongation which occurs when a dry residue is hydrated.

It may be noted that, at constant tension f, l is a linear function of x. Thus, the elongation isotherm can be expected to be proportional to x, the number of molecules adsorbed on strong bonding sites, rather than to α.

The effect of tension may now be noted also. From the isotherm it can be seen that an increase in β at constant B, γ, and η causes a decrease in the amount adsorbed at a given relative humidity. From the definition of β it will be seen that β will increase with increases in tension if $\frac{f^2\omega_2}{2\psi_2 kT} > \frac{f^2\omega_1}{2\psi_1 kT}$. This requires either that $\omega_2 > \omega_1$ or $\psi_2 < \psi_1$ or both. Both of these possibilities are plausible in terms of the general knowledge of the effects of water on the properties of fibers.

Application of the Theory

The theory just derived makes no allowance for hysteresis and hence, strictly speaking, cannot be applied to isotherms showing hysteresis. The isotherms for hair at 2 grams and 1 gram tension obtained after the fiber had been through an isotherm at 5 grams tension show little or no hysteresis (see Figures 5 and 6). The theory is applied to these isotherms and also to the isotherm at 5 grams tension, which shows considerable hysteresis. The application of the theory to the isotherm at 5 grams tension is made to emphasize the effects of tension and to give an indication of the nature of hysteretic effects. Hysteresis will be discussed more fully in a later paper.

Figure 8 shows the application of the theory to the last three adsorption isotherms of Figure 7. Since what is known of the structure of hair indicates infrequent cross-bonds, and a rough order-of-magnitude test on the experimental data indicates that γ is probably small, only the η term is used for the free-energy term for swelling the fiber network. The three curves are fitted using B and η constant and varying β. The results in Figure 8 constitute an adequate fit of the data.

Equation (29) shows a twofold influence of tension on elongation. The tension changes the value of x, in this case decreasing it since β increases with tension, and increases the elongation of the wet and dry residues. Actually, the spring constant for the dry residues which can be evaluated independently is so large that, if the initial length is taken as the dry length under the given tension rather than under no tension, the first term of equation (29) can be ignored. The decrease in x and the increase in deformation per residue work against one another and tend to make the elongation changes roughly independent of the tension, as is known to be the case experimentally. Figure 9 shows the application of equation (29) to the data on hair. The 100% R.H. points on the curves for 1-gram and 2-gram loads are used to determine the constants

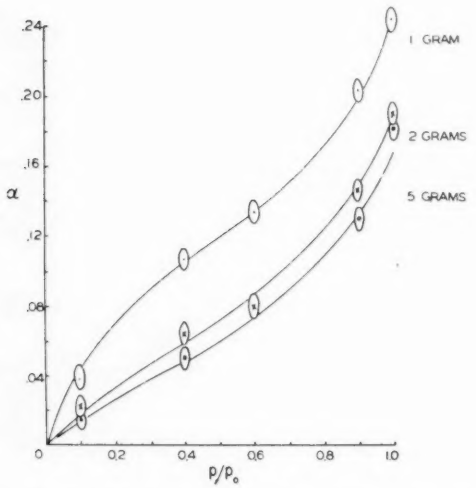

FIG. 8. *Comparison of theoretical adsorption isotherms for hair under tension with isotherms derived from swelling data.*

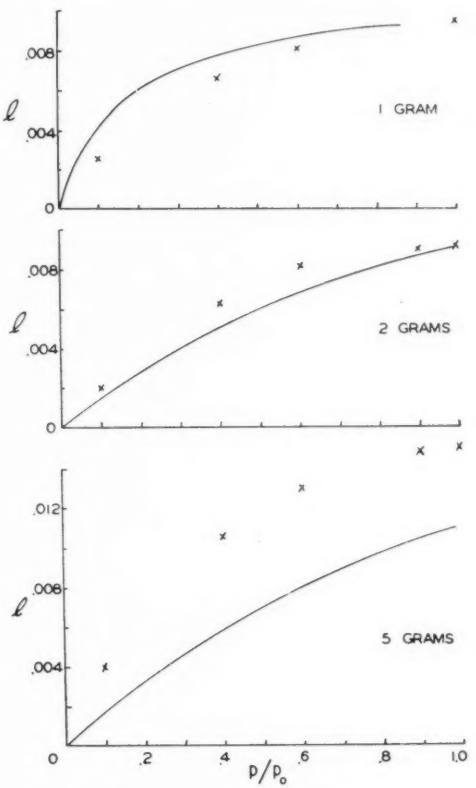

FIG. 9. *Experimental and theoretical elongation isotherms for hair under tension.*
x *experimental,* —— *theoretical*

TABLE III

Load	B	β	η	l_{12}	ψ_2	$\left(-\frac{f}{\psi_1}+l_{12}+\frac{f}{\psi_2}\right)$
1 g.	.105	.07	.82	.0090	1.90×10^{10}	.097
2 g.	.105	.30	.82	.0090	1.90×10^{10}	.108
5 g.	.105	.42	.82	.0090	1.90×10^{10}	.141

in the elongation equation. The fits of the theory with the data are of the right order of magnitude for the 1-gram and 2-gram loads, but definitely low in the case of the 5-gram load. The constants used are summarized in Table III.

Considering only the isotherms for the 1-gram and 2-gram loads, there are 4 experimental curves and 8 constants. One of these, ψ_1, is evaluated independently, and another, A, is necessary only if the evaluation of ψ_2 and l_{12} is desired. Furthermore, A can, in many cases, be set equal to B. This leaves 6 adjustable parameters for 4 curves. From this point of view the test of the theoretical equation is considerably more severe than the fitting of an adsorption isotherm with 3 adjustable parameters.

The values of l_{12} and ψ_2 in Table III are derived on the basis of $A = B = 0.105$. l_{12} corresponds to a 1% elongation on hydration and is smaller than might be expected. The values of $\psi_1 = 5.7 \times 10^{10}$ dynes/cm² and $\psi_2 = 1.9 \times 10^{10}$ dynes/cm² can be compared with values estimated from stress-strain curves at various humidities on wool obtained by Speakman [26], which are $\psi = 4.9 \times 10^{10}$ dynes/cm² at 0% relative humidity and 2.0×10^{10} dynes/cm² at 100% relative humidity. A direct measurement in this laboratory on hair at 60% relative humidity gave $\psi = 4.0 \times 10^{10}$ dynes/cm². Thus, the moduli found agree well with independent experimental evidence.

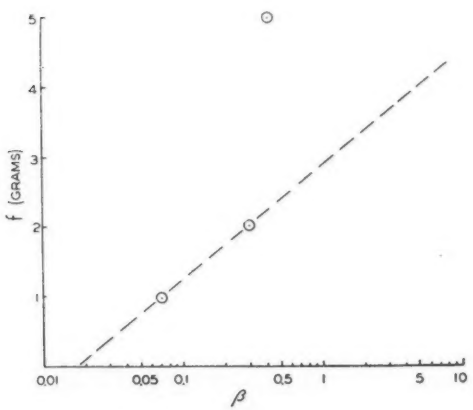

FIG. 10. *Dependence of β upon force.*

Independent estimates of the value of η do not seem profitable because of the approximations involved.

In the simple theory, a plot of log β vs. f should give a straight line. Figure 10 gives such a plot. A straight line through the 1-gram and 2-gram points would give a value for β of about 20 for the hairs under a 5-gram load, indicating conditions highly unfavorable for adsorption on the fixed sites since $\beta = 1$ represents the condition for liquid condensation. A line through the 1-gram and 5-gram points would give a value of β under no tension close to that at 1-gram tension. This is qualitatively in agreement with the data in Figures 2 and 3, which show small differences between the swelling isotherms under no load and under 1-gram load. It is evident that the simple relationship does not hold but that more information is needed to determine whether the error is experimental or theoretical in nature.

White and Eyring [29] have discussed the relationship of B to the chemical composition of the fiber involved. In general, values of B are considerably less than would be expected from stoichiometric considerations. Chemical evidence is lacking on the exact constitution of hair. However, if an estimate of 126 is made for the mean residue weight (see [29]), considering hair to be identical with wool, and the number of polar side chains is estimated at 341 moles/10^5 g. [23], about half of the total polar sites (counting one per residue in addition to those on polar side chains) is used. Furthermore, $A \cong 1.2B$, the number of polar side chains in B helping to cancel the error caused by some of the chemically possible sites not being available. This means that l_{12} is actually some-

what larger than the value given. Finally, a comparison of η with values of log p/p_o at low relative humidities shows that the small volume contraction occurring at small regains will have a negligible effect on the constants of the adsorption isotherm.

Discussion

The calculation of the free energy of swelling of the adsorbent network bears certain similarities to the calculations made in the case of the swelling of rubber by non-polar solvents. In both cases, ideal networks are postulated which are assumed to be thermodynamically equivalent to the actual network and the thermodynamic properties of the ideal network determined. In the case discussed here a purely mechanical model in which the entire fiber acts as an entity is used. This is similar to the use of a mechanical model consisting of elastic threads for rubber. The elastic-thread model has been shown to give stress-strain properties which are functionally similar to those derived from the more sophisticated kinetic theory of elasticity [21]. The kinetic theory of elasticity relies on the essential independence of the elementary chain segments to give it enough mathematical simplicity to be useful. This assumption probably cannot be made in the case of fibers, thus increasing the difficulty of calculating a partition function for the network in terms of the properties of the individual segments. It should be stressed that the use of the individual segments has merely proved to be a convenience in previous work and that any reasonable unit, including the fiber as a whole in the case of a three-dimensional polymer, may be used if properly treated.

However, a more serious difficulty presents itself. The use of an ideal network implies an averaging-out of all physical and chemical heterogeneities in the actual network other than those which may be specifically introduced in the design of the ideal network. The physical heterogeneity of fibrous materials is particularly important. The recent work of P. H. Hermans and coworkers [18] makes it clear that cellulosic fibers at least do not deform uniformly throughout when swollen or stressed externally, the crystalline portions acting differently from the amorphous portions. More data are needed before the differences between fibers and within an individual fiber can be understood. As has been discussed by White and Eyring [29] and will be discussed in a later paper, adsorption and swelling hysteresis can also be attributed to this physical heterogeneity.

Chemical heterogeneity will introduce a spectrum of values for β. Furthermore, the presence of polar side chains will lead to a lack of correspondence between the constants A and B. Evidence on chemical heterogeneity and the various values of β can be obtained from chemical modification experiments such as those of Hoover and coworkers [22]. Again, however, enough data are not available to treat this complication at the present time.

Finally, the assumptions and the derivation of the B.E.T. equation itself must be discussed. The work of Hill shows most clearly that the B.E.T. assumptions lead to a physical picture of the adsorbed molecules rising in rods from the surface (see, however, the discussion below). The length of the rods depends upon the number of molecules adsorbed on top of a given first-layer molecule. This picture is obviously a first approximation. The method of introducing the multilayers is oversimplified, as has been shown by Hill [19], Halsey [15], and others who have considered possible effects of interaction between adsorbed molecules and of non-uniform surfaces. In fact, a completely non-uniform surface would give a monolayer isotherm the shape of which would be dependent upon the relative proportions of each type of site and which could be sigmoid. Thus, as much experimental evidence as possible must be considered in deciding which variant of multilayer or monolayer theory must be used for a particular adsorbent and gas or vapor.

In adsorption throughout the bulk of a fiber, slightly different conditions prevail from those on a surface. Criticisms based on the existence of a uniform surface and the subsequent probability of close packing between layers are no longer valid. The condition imposed by the configurational term in Hill's derivation of the B.E.T. equation is not, in its broadest interpretation, that of a rod-like arrangement but of any arrangement in which the adsorption of the $(n+1)^{th}$ molecule on a given site is dependent upon the n^{th} molecule already being adsorbed. In other words, any form of cluster is satisfactory providing that the second molecule adsorbed always is adsorbed on a fixed position with respect to the first, and so forth, for subsequent molecules. These restrictions make the use of the simple B.E.T. picture in which the multilayer molecules are in a state similar to the liquid state incor-

rect but do not eliminate some of the isotherms considered by Dole. However, the simple B.E.T. equation is probably a good enough approximation to determine effects of tension, structure, etc., as has been done here. The problem in which the second molecule has n possible positions with respect to the first, the third, $n - 1$, and so on until the n^{th} molecule is adsorbed into the cluster, can be solved in principle but leads to n^{th}-degree algebraic equations which are difficult to solve.

Finally, of course, mixing, such as has been suggested by Barrer, and a graded series of sites varying in heat of adsorption, such as have been suggested by Halsey, are possible. The data presented here on the anisotropy of swelling and the effects of tension make attractive the hypotheses that the number of secondary sites is dependent upon the number of filled primary sites and that the secondary sites differ in kind from the primary sites. However, although the sufficiency of the theory introduced here has probably been adequately shown, its necessity has not been, and it is possible that another series of physically plausible assumptions leads to the same experimental results.

In summary, it may be stated that a theory using multilayer adsorption on sites within an extremely anisotropic network of semi-rigid molecules gives quantitative agreement, within the limitations imposed by hysteretic effects, for the adsorption of water on hair. It also gives the observed swelling isotherms to a fair approximation. At the other extreme, a theory of free mixing of adsorbate with an isotropic network composed of independent molecular segments has been successfully applied to the adsorption of non-polar liquids by rubbers [11, 12]. Most swelling materials will fall between these two limits and the theoretical approach necessary for a successful interpretation of the adsorption data will be conditioned by collateral knowledge of the molecular structure of the material and by swelling data, especially anisotropy data, such as are given here.

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Water Sorption and the Poly-Phase Structure of Cellulose Fibers*

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Abstract

Many of the methods used to study the fine structure of cellulose are tedious and not suitable for routine use. In the present work, an equilibrium moisture regain method which can be carried out on a large scale with a high degree of accuracy has been developed. The method is illustrated by a wide variety of cellulose materials covering a wide range of moisture sorption capacity. The terms "accessibility" and "crystallinity" are discussed and possible errors arising from assumed equivalence of these terms are pointed out. A preliminary attempt to evaluate both accessibility and crystallinity of cellulose from moisture regain data has been made. This evaluation results in a proposed revision of the scale of reported crystallinities of various types of cellulose.

The hydrolysis method for studying cellulose accessibility has been compared with moisture regain and x-ray diffraction methods. It is proposed that recrystallization of cellulose during hydrolysis is a determining factor in this method and, therefore, that published data obtained from hydrolytic studies should be reconsidered.

MANY METHODS have been proposed and used for the measurement of the average degree of crystallinity or lateral order of cellulose. These methods may be classified as:

(*A*) *Chemical methods*, which include the hydrolysis and catalytic oxidation method as used by Nickerson and coworkers [25, 26] and as modified by Conrad and Scroggie [9] and Philipp [27], the use of mild acid hydrolysis with accompanying changes in D.P. [4], the thallation method [1], and oxidation methods [14].

(*B*) *Physical methods*, which include the rate of exchange of deuterium oxide [3, 13], x-ray diffraction [16, 21], density [16], calorimetry [22], and sorption [16, 18].

None of these methods is absolute, but in most cases it has been possible to classify different celluloses according to the relative amounts of crystalline material.

Although the moisture sorption of cellulose has been widely discussed in the literature [7, 30, 31, 32, 33, 34, 35] and, according to modern views, the sorptive capacity may be associated with the order-disorder structure of cellulose, only a few attempts have been made to correlate sorption data with cellulose structure. The concepts of Brunauer, Emmett, and Teller [6] have been applied to this problem [2, 11, 28] but the method is unwieldy for routine use. More recently, Hermans [16 (pp. 50–52)] has concluded that as a first approximation there is a direct relationship between the capacity of a fiber for moisture sorption and the quantity of amorphous material in the fiber. This hypothesis has not been thoroughly defined to account for possible differences in crystal size or crystal perfection in different celluloses, but it seems to offer a good basis for rapid, accurate estimation of the average "crystallinity" or lateral order of cellulose fibers.

In this work, the relative moisture sorptive capacities of various cellulose fibers are reported. The expression of sorptive capacity in terms of parameters relating to the fine structure of cellulose has been undertaken. Differences between the hydrolytic and physical methods of determining cellulose crystallinity are discussed and a mechanism based upon moisture regain data has been proposed to account for the observed discrepancies.

Experimental Methods

Since all the determinations of cellulose accessibility are relative, no attempt has been made to place the method on an absolute scale, and the following procedure for the determination of moisture

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TABLE I. Correction Factor for Moisture Regain

Sample	Run no.	Regain of control (%)	Correction factor	Regain of sample (%)	Corrected regain of sample
Viscose rayon (young viscose)	1	10.91	1.138	11.90	13.54
	2	9.08	1.368	9.91	13.56
	3	12.21	1.016	13.38	13.60
	4	11.91	1.041	13.04	13.59
	5	10.77	1.153	11.81	13.63
Viscose rayon (old viscose)	1	10.88	1.140	10.71	12.22
	2	12.85	.967	12.65	12.21
	3	12.08	1.028	11.90	12.23
	4	10.79	1.151	10.53	12.11
Wood pulp	1	10.68	1.162	6.86	7.98
	2	10.34	1.200	6.58	7.90
	3	10.70	1.160	6.89	7.99
	4	10.77	1.153	7.06	8.15

sorption was adopted: One-gram samples were placed in small weighing bottles and dried in a laboratory oven for 5 hours at 105°C. The bottles were closed as soon as the oven was opened, cooled for 30 minutes, and weighed accurately to within ±0.2 milligram. The samples were conditioned to constant weight in a room maintained at 58 ± 1 percent relative humidity and 75 ± 1°F. The percent moisture regain was calculated in all cases on the basis of the oven-dry sample weight. After conditions for the establishment of equilibrium were studied, it was not necessary to weigh to constant weight, but the weight after a given conditioning time was used. For example, in the conditioned room used, 120 hours' conditioning was found to be sufficient for yarn samples. For more compact samples, longer times, depending upon the nature of the sample, are necessary.

The inaccuracy of oven drying at 105°C and the variation of humidity and temperature in the conditioning room make reproducibility very poor over a period of time. Therefore, a standard sample was run with each set of samples on which the moisture regain was to be determined. The moisture regain of this standard sample was arbitrarily set at 12.41 percent, obtained from an average of sixteen determinations. A correction was then applied to each set of samples for the deviation of the measured regain of the control sample from the standard regain. The correction is applied as follows:

$$\text{Measured regain of sample} \times \frac{12.41}{\text{Measured regain of control}} = \text{Corrected regain of sample.}$$

After correction, a set of relative moisture regain values may be assembled which will have a standard deviation of about 0.07 percent. Although the control sample used in this work was a rayon, the correction is valid for both native and regenerated celluloses. The correction factor and the reproducibility are illustrated in Table I. Extreme cases are given to show the applicability of the correction over a wide range of determined values of the moisture regain. The normal variation of the control sample regain is of the order of ±0.3 percent.

In most cases the determined value of the regain of the control sample is lower than the standard value of 12.41 percent and therefore the corrected regain values are too high. This error in absolute value is not of great importance since only a relative scale is required. The whole series of determinations could be placed on an absolute scale by determining the moisture regain of the control sample accurately and correcting all others to this base regain. For example, using more standard drying conditions and controlling relative humidity by standard sulfuric acid, reproducible results can be obtained on different runs without the use of a control sample. Such a procedure requires more attention, but is more applicable when a high degree of accuracy is required.

Densities were determined by the procedure of Hermans [17], which consists of drying the fibers completely at 100°C in dry air and distilling carbon tetrachloride into the sample chamber. The density was found by determining the temperature at which the fiber remained suspended in the carbon tetrachloride. This temperature is usually between 40° and 70°C. All density values were then corrected

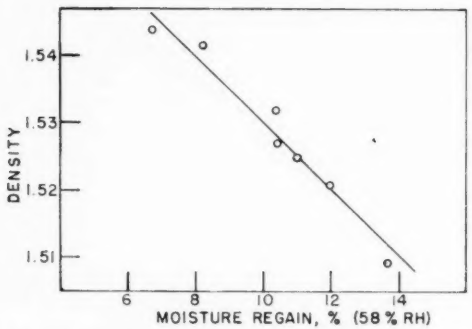

FIG. 1. *Probable relationship between density and moisture regain of cellulose fibers.*

to 20° C, using the coefficient of dilation of cellulose (8×10^{-5}) as given by Davidson [10].

Results and Discussion

Moisture regain, sorption ratio, and density data for a series of cellulose samples which were picked to cover a wide range are given in Table II. The sorption ratio is the ratio of the moisture regain of the sample in question to that of cotton when both regains are determined under the same conditions of relative humidity and temperature (58% R.H. and 75° ± 1°F). The cross plot of these data in Figure 1 shows a fairly good linear relationship between the density and moisture regain of the cellulose samples. These results are in good agreement with those of Hermans [16] on which he based his conclusions (1) that differences in density of cellulose fiber can be attributed to differences in relative amounts of crystalline material, (2) that there is a close parallelism between density and moisture sorptive capacity, and (3) that as a first approximation there is a direct relationship between the sorptive capacity and the quantity of amorphous material in the fiber.

On the basis of these premises, either the moisture regain or the sorption ratio should give directly a relative crystallinity scale for cellulose fibers, and according to the data in Table II high-tenacity rayon would contain about twice as much amorphous material as does cotton.

However, the present theories of sorption and the known behavior of cellulose will not allow a strict proportionality between moisture regain and the quantity of amorphous cellulose in a fiber. Hermans [16, 19] first postulated this departure from linearity on the basis of x-ray studies of cellulose fibers at different moisture contents. He concluded that crystalline regions of cellulose II (regenerated fibers) form a true hydrate ($C_6H_{10}O_5 \cdot {}^1/_3\ H_2O$ or $C_6H_{10}O_5 \cdot {}^1/_2\ H_2O$) on sorption of water vapor, while crystalline regions of cellulose I (native fibers) do not form hydrates. Therefore, for a given amount of amorphous material, a fiber containing crystalline cellulose II will have a higher sorptive capacity than a fiber containing crystalline cellulose I.

According to present theories of sorption, the first strong sorption of water by cellulose is caused by hydrogen bonding of water molecules to the accessible hydroxyl groups which act as sorption sites [33]. Since cellulose is composed of easily accessible amorphous regions and less accessible crystalline regions, it is probable that these accessible hydroxyl groups may be either in the amorphous areas or in the surface of a crystalline area. The contribution of the crystal surface hydroxyls to the total regain cannot be ignored, for the crystalline areas are small and therefore have a large percentage of their hydroxyls in the surface. Furthermore, the total percentage of the hydroxyls in a crystal which lie in the surface will increase with decreasing crystal size and, therefore, the contribution of the sorption on crystal surface to the total amount of sorbed water will increase with decreasing crystal size, and for two celluloses containing equal amounts of amorphous material that sample with the smaller crystal size will exhibit the higher moisture sorptive capacity.

Therefore, although the sorptive power of a cellulose fiber is, among other things, a function of the number of hydroxyl groups capable of acting as sorption centers because of their position in the polycrystalline cellulose structure, the interpretation of sorptive power in terms of amorphous cellulose must be qualified, for apparently these sorption-active

TABLE II. MOISTURE REGAIN AND DENSITY OF CELLULOSE FIBERS

Sample	Moisture regain (58% R.H.)	Sorption ratio	Density (20°C)
Cotton	6.70	1.00	1.544
Wood pulp	8.05	1.20	1.541
Fortisan	9.60	1.43	—
Mercerized wood pulp	10.45	1.56	1.534
Fiber G	11.00	1.64	1.525
Experimental rayon	11.50	1.71	—
Textile rayon	12.00	1.79	1.522
High-tenacity rayon	13.25	1.98	1.509

groups may lie in either amorphous or crystalline regions. The best modification of this interpretation seems to lie in the concept of "accessibility," in agreement with the terminology used by other authors [1, 9, 13]. The accessibility of a cellulose fiber is usually defined as that fraction of total cellulose which is available for reaction with a given reagent under certain specified conditions, such as concentration, time, and temperature. The experimental values of accessibility are dependent upon the size and polarity of the molecule used and upon the degree of swelling of the cellulose in the medium used in the determination, but for any given set of conditions the accessibility of a cellulose can be determined as an exact empirical value. Unfortunately, the mechanism of sorption of water by cellulose is not well enough defined to allow a direct determination of the percentage of accessible cellulose. In fact, if such a direct determination were possible, it would apply only to a definite moisture content value, for additional sorption sites are probably formed as the cellulose swells on addition of water. However, it seems reasonable to assume that the moisture regain of cellulose at 58 percent relative humidity is proportional to the general accessibility of the fiber to water and, therefore, that the moisture regain of cellulose offers directly a relative scale of cellulose accessibility. From the theory presented above, this accessibility will be a function not only of the relative amounts of crystalline and amorphous areas but also of the crystal size and the ability of water to penetrate the crystalline region. This concept has the advantage that it does not arbitrarily require that a cellulose of high regain be highly amorphous in character, but it permits the interpretation that a high regain may be obtained from a crystalline cellulose of small crystal size.

From published data on cellulose accessibility, crystal size, and hydrate formation it is now possible

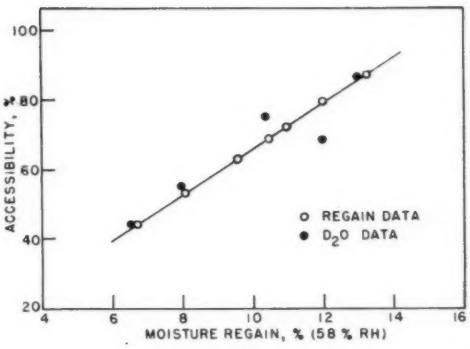

FIG. 2. *Probable relationship between the moisture regain and accessibility of cellulose fibers.*

to check the validity of the accessibility-moisture regain relationship and to estimate the magnitude of the effect of crystal size on the apparent crystallinity of cellulose fibers. The accessibility data of Frilette, Hanle, and Mark [13] seem to be the most typical and comprehensive and are reproduced in the first two columns of Table III. The deuterium oxide accessibility is expressed as the fraction of the cellulose hydroxyls which will exchange with deuterium oxide in 4 hours. Assuming that Mark's value for cotton is correct, the accessibility values in column 3 were calculated by multiplying Mark's value (cotton = 44) by the sorption ratio of each sample as given in Table II. The agreement between the accessibilities calculated from moisture regain data and those from the deuterium oxide values is very good in view of the fact that the samples used in this work and those used by Frilette were from different sources and may have had different histories. This probable linear relationship between accessibility and moisture regain of cellulose is illustrated in Figure 2. Although Mark gave no moisture regain data, his accessibility

TABLE III. CORRELATION OF D_2O EXCHANGE AND MOISTURE REGAINS

Sample	D_2O exchange		Moisture regain	
	% Accessibility	% Crystallinity	% Accessibility	% Crystallinity
Cotton	44	78	44	78
Wood pulp	55	63	53	65
Fortisan	—	—	63	51
Mercerized wood pulp	74	36	69	43
Fiber G	67	46	72	39
Experimental rayon	—	—	75	35
Textile rayon	68	45	79	29
High-tenacity rayon	86	20	87	18

data have been plotted for illustrative purposes by assigning generally accepted values for the moisture regain of his samples. It should be noted that the deuterium oxide method measured the accessibility of cellulose in water—*i.e.*, the accessibility of swollen celluloses. Therefore, the moisture regain accessibilities obtained by calculations such as those above can be considered absolute only for cellulose which is completely swollen in water, because as water is removed from its points of bonding to cellulose the accessibility will decrease. However, the ratios of the moisture regains of different celluloses observed at 58 percent relative humidity are present in the same order and are of essentially the same magnitude over the complete range from zero to 100 percent relative humidity. It seems safe to conclude that the materials will have the same relative order of accessibility in the dry condition as is given in Table III, with a change only in degree of accessibility.

Since accessibility is usually an exact experimental quantity, it is more reasonable to use "accessibility" than "crystallinity" to describe different celluloses. However, it has been common practice to convert accessibility into "percent crystallinity" and, indeed, such conversions are informative not only for evaluating methods of study but also for the ultimate interpretation of cellulose properties as functions of cellulose structure. According to Mark [13], the relationship between crystallinity and accessibility may be written

$$A = \sigma\alpha + (100 - \alpha), \qquad (1)$$

where A = the percentage of all the hydroxyls which react rapidly with D_2O,

σ = the fraction of the accessible hydroxyls which lie in crystalline domains,

and

α = the percent of crystalline cellulose in the sample.

Solving for α:

$$\alpha = \frac{100 - A}{1 - \sigma}.$$

The estimated value of α is dependent upon the method of determining A and upon the value assigned to σ. Assuming a constant crystal size, Mark [13] has, as a first approximation, calculated that 28 percent of the hydroxyls in a cellulose crystal are on the surface. If all these hydroxyls are reactive, the value of σ will be 0.28. The percent crystalline material calculated from this value of σ is listed in column 2 of Table III for Mark's data and in column 4 for the calculated moisture regain accessibilities. The reason for the difference in order of mercerized wood pulp and Fiber G by the two methods is not apparent, but probably lies in the extreme dependency of the properties of mercerized pulps on the method of mercerization, washing, and drying.

It seems possible to refine the first approximation of percent crystallinity from accessibility values as given above by assigning different values of σ to different celluloses on the basis of known data for the various types of cellulose and their probable structures. This has been done by combining data on crystal size, the hydration of crystals, and an assumed mechanism by which water is bonded in the cellulose fiber. From the literature and present theories of cellulose structure the following assumptions seem to be most worthy of consideration: (1) the average crystals in native cellulose are about 50 Å. in breadth, while in regenerated cellulose the average crystal breadth is about 25 Å.; (2) regenerated cellulose crystalline regions, when completely hydrated, contain ½ water molecule per anhydroglucose unit, while native cellulose crystalline regions are inaccessible beyond the surface; (3) amorphous cellulose contains, on the average, 1½ water molecules per anhydroglucose unit when completely hydrated; (4) and, on the average, one-half of the hydroxyls on chains lying in a crystal surface are accessible and will behave as amorphous cellulose hydroxyls.

The assumption for crystal size is approximated from low-angle x-ray scattering data of Fankuchen [12] and Guinier [15], and from electron microscope data of Morehead [24] on hydrolyzed cellulose residues. The values for accessibility of regenerated cellulose crystals are taken from data of Hermans [16, 19], who suggests that either ⅓ or ½ molecule of water per glucose unit is bound within the crystallite. The mechanism of bonding in the amorphous regions results from the work of Hermans [16], Champetier [8], Tankard [29], and others who have concluded that in wet cellulose about 0.5-molecule of water is bound per molecule of glucose residue in native celluloses and about 1.1 molecules of water per molecule of glucose residue in regenerated celluloses. If, as a first approximation, native and regenerated celluloses are assumed to be about 40 and 80 percent accessible to water (as determined by Mark), these figures correspond to approximately 1.2–1.4 molecules of bound water per molecule of accessible glucose residue. Hermans [19] postulated two hydrates of cellulose, $C_6H_{10}O_5 \cdot 1\frac{1}{3}\ H_2O$ and $C_6H_{10}O_5 \cdot 1\frac{1}{2}$

TABLE IV. EFFECT OF CRYSTAL SIZE AND HYDRATE FORMATION ON % CRYSTALLINE CELLULOSE

	% Accessibility	% Crystallinity			
		$\sigma = 0.17$	$\sigma_N = 0.17$ $\sigma_R = 0.28$	$\sigma_N = 0.17$ $\sigma_R = 0.44$	$\sigma_N = 0.17$ $\sigma_R = 0.52$
Cotton	44	67	67	67	67
Wood pulp	53	57	57	57	57
Fortisan	63	45	51	66	77
Mercerized wood pulp	69	37	43	55	65
Fiber G	72	33	39	50	58
Experimental rayon	75	30	35	45	52
Textile rayon	79	25	29	37	44
High-tenacity rayon	87	16	18	23	27

H_2O, which fit this range, but he was unable to prove which was the more probable. The ratio $C_6H_{10}O_5 \cdot 1\frac{1}{2}\ H_2O$ was arbitrarily chosen.

On the basis of these assumptions it is possible to calculate an effective crystallinity which is partially corrected for differences in the accessibility arising from differences in crystal structure and crystal size. Because of the approximate nature of the assumptions, values have been assigned for different combinations of the crystal and hydration assumptions so that individual evaluation of each assumption could be made. For example, in a native cellulose crystal 50 A. wide about 17 percent of the hydroxyls are on the surface and available for sorption of water. Using the same terminology given by Mark for equation (1), σ is 0.17 and the crystalline fraction is related to the accessibility by the the equation

$$\alpha = \frac{100 - A}{0.83},$$

which is the equivalent of Mark's equation and differs from it only in differences in assumption concerning the accessibility of the crystal surface hydroxyls. Crystallinity values calculated from this equation are listed in Table IV, column 2, to establish a base for comparison of crystal size effects. This value for σ is based on native cellulose crystals and will be designated as σ_N in contrast to values of σ_R for regenerated crystals. In regenerated cellulose crystals 50 A. wide 17 percent of the hydroxyls will be on the surface and, on the assumption that in the crystal 1 water molecule is bonded for each 6 hydroxyls, each of the remaining hydroxyls within the crystal itself can be considered 33 percent accessible. This is equivalent to the total accessibility of 33 percent of the hydroxyls within the crystal, or 28 percent of all the hydroxyls, and yields a value for σ_R of 0.44. The crystalline fraction is then expressed by the equation

$$\alpha = \frac{100 - A}{0.56}.$$

Similarly, it can be shown that for regenerated cellulose crystals 25 A. wide the σ_R value will be 0.28 if no crystal hydrate formation takes place, or 0.52 if crystal hydration takes place (according to assumption 2).

Using these values for σ_R, crystallinity values have been calculated and are listed in Table IV. Column 3 illustrates the effect of crystal size alone, column 4 illustrates the effect of crystal hydration alone, and column 5 illustrates the effect of both crystal size and hydration on the calculated crystallinity value. On the basis of existing data it is not possible to decide upon any one of these last three columns of data as giving the most probable values for the degree of crystallinity of different celluloses. However, the trend is unmistakable that on the basis of present data and theory of cellulose structure a large portion of the high reactivity, moisture sorption and other properties of regenerated cellulose is directly traceable to the smaller crystal size and/or higher accessibility of the crystalline domains present rather than entirely due to differences in amount of crystalline material present, as has been most frequently assumed.

None of these values can be taken as final, but they do not conflict with the known behavior of cellulose fibers. The data on which the assumptions involved are based are somewhat indefinite and revision will undoubtedly be necessary as new data become available. The crystal-size assumption for native and regenerated celluloses is at least in the right direction, for the conditions involved in plant growth and in rayon spinning are such that regenerated fibers would be expected to have smaller crystalline regions. However, the calculated crystallinity values given in

column 5 of Table IV seem to be somewhat inconsistent with theoretical considerations. For example, the value for Fortisan seems quite high, and it is not likely that mercerized wood pulp would contain a higher percentage of crystalline material than the original pulp. From the calculated values in columns 3 and 4 these discrepancies arise from the assumption that regenerated cellulose crystals form hydrates. It is strange that crystalline regions of regenerated cellulose would form hydrates while those of native cellulose would not. The original hypothesis of hydrate formation is based on an observed lattice expansion of regenerated cellulose crystals as water is sorbed, but it does not seem to be the only interpretation allowed by the x-ray data. The samples used in the determination of lattice expansion were mercerized ramie fibers in which all different degrees of crystallization are probable. It is quite possible that imperfect crystals are present which will form hydrates and still give coherent x-ray scattering. If this is true, one would expect to find a lattice expansion in both native and regenerated fibers on wetting in roughly an inverse proportion to the accessibility of the fibers. In this respect it would be of interest to study the lattice expansion of cellulose samples which have been treated to remove the amorphous regions so that only the most perfect crystalline structures remain.

Effect of Hydrolysis on Accessibility

Published crystallinity and accessibility data such as those given in Table V show a wide variation of values for similar samples studied by different methods, which makes interpretation in terms of cellulose structure difficult. However, one distinct discrepancy in these data is apparent. The hydrolysis methods as a class give higher values for the percentage of crystalline cellulose than do the physical methods. This trend seems generally true for other chemical methods—such as thallation [1], oxidation [14], and acetylation [23]. In the case of thallation or acetylation this trend can be attributed to the fact that the media used do not swell cellulose appreciably, but the discrepancy between such methods as deuterium oxide exchange and hydrolytic degradation is not so apparent because both employ aqueous media, in which the swelling of cellulose should be fairly comparable with that in water. For example, one sample of textile rayon showed cross-sectional swellings of 63, 62, and 63 percent; and another, 67, 66, and 70 percent in water, 2.5*N* HCl, and 5.0*N* HCl, respectively. Since there is no reason to expect that D_2O in water should greatly affect cellulose swelling, there seems to be little possibility that the large observed differences in accessibility can be due to differences between the swelling of cellulose in aqueous D_2O, dilute mineral acids, and water. Therefore, on the theory that this discrepancy probably arose from the fact that hydrolysis methods utilize a chain cleavage mechanism with subsequent removal of short chains, the accessibility and crystallinity of hydrocelluloses were studied by moisture regain and x-ray diffraction methods. The results of these studies indicate that the low accessibility values as determined by hydrolysis are partially accounted for by recrystallization which accompanies chain cleavage in an aqueous medium at elevated temperatures. This recrystallization is evident in that the moisture regain of hydrolyzed cellulose decreases much faster than weight is lost in the early stages of hydrolysis. Data obtained for a highly accessible viscose rayon in 5*N* HCl at 50°C are shown in Table VI. If, as is usually done in the literature, the change in moisture regain of the hydrolyzed cellulose is attributed solely to the small loss of amorphous cellulose indicated in the table, each glucose unit which is removed would

TABLE V. THE PERCENT "CRYSTALLINITY" OF CELLULOSE

Method	Cotton	Wood pulp	Mercerized cotton	High-tenacity rayon
Hydrolysis method				
Nickerson [25, 26]	94	90	89	79
Conrad and Scroggie [9]	92–94	88–91	85–89	69–73
Philipp [27]	88	—	82	67
X-ray diffraction [20]	69	—	—	39
Density [16]	58	53	40	24–32
Calorimetry [22]	87	—	77	52
Deuterium oxide exchange [13]	78	63	—	20

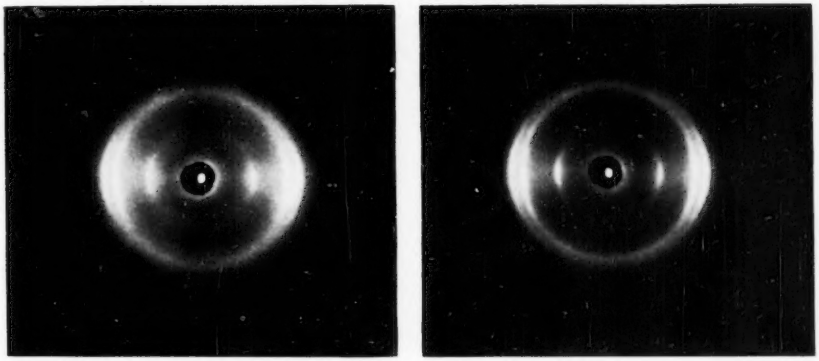

FIG. 3. *X-ray diagrams of (a) (left) untreated rayon and (b) (right) the same sample hydrolyzed in 5N HCl at 50° C for 1 hour.*

have to have been associated with from 20 to 40 molecules of water in the original cellulose. This ratio of water to glucose is unreasonable and therefore the data are interpreted as an indication that crystallization has taken place during hydrolysis.

Early x-ray workers found that hydrolytic degradation of cellulose produced no change in the crystal structure and concluded that the reactions were confined to the amorphous regions. More recently, Ingersoll [21] has shown that short treatments in boiling hydrochloric acid greatly increase the definition of the x-ray diagram and has suggested that this effect could be due to chain rearrangement after chain cleavage with a subsequent actual increase in lateral order or crystallinity of the sample. However, this x-ray behavior alone can be explained by a mechanism of removal of amorphous regions on the basis that a perfect crystalline cellulose will give a sharper x-ray diagram than a 50-50 mixture of crystalline and amorphous cellulose. To clarify these alternative explanations, x-ray diffraction studies were made of hydrocelluloses similar to those shown in Table VI for which the moisture regains and the loss in weight are known. X-ray diagrams of these materials show that the crystallinity or lateral order does increase on hydrolysis and that the major part of this increase in crystallinity occurs with a loss in weight of less than 1.5 percent. Typical diagrams are shown in Figure 3, in which the change in x-ray diagram illustrated occurs with only a 0.7 percent loss in weight on hydrolysis. This extreme change in the x-ray diagrams occurring with only slight loss in weight on hydrolysis also supports the recrystallization mechanism.

TABLE VI. WEIGHT LOSS AND CHANGE IN MOISTURE REGAIN ON HYDROLYSIS

Hydrolysis time (min.)	Moisture regain	Weight loss (%)	Mols. H_2O/ mol. glucose lost
0	13.35	—	—
30	11.42	.43	41
60	10.56	.67	37
90	10.18	.91	31
120	9.86	1.42	22

The question arises as to whether this recrystallization occurs during the hydrolysis itself or merely upon drying of the swollen sample. X-ray diagrams were made of hydrolyzed samples which were washed with cold water and kept wet during x-ray exposure. These diagrams indicate that the crystallization occurs in the hydrolyzing medium before the sample is dried, for in all cases the x-ray diagrams of the wet hydrocellulose show the same distinct change as that illustrated in Figure 3 for air-dry samples. Similarly, pretreatment of the samples with water alone at 50°C before hydrolysis caused no appreciable change in either the x-ray diagram or the moisture regain of the samples. These combined hydrolysis, moisture regain, and x-ray diffraction data offer conclusive evidence that recrystallization of cellulose does occur in the aqueous media normally used for hydrolytic studies. Most of this crystallization occurs within 1 or 2 hours in 5*N* HCl at 50°C, as indicated by the fact that the x-ray diagram changes

TABLE VII. PERCENT "CRYSTALLINITY" OF CELLULOSE (NICKERSON) CORRECTION FOR CRYSTALLIZATION ACCOMPANYING HYDROLYSIS

Sample	% Crystalline cellulose (Nickerson)	Reactivity of crystalline portion	Moisture regain		% Cellulose crystallized in hydrolysis	% Crystalline cellulose (corrected)
			Untreated	Hydrolyzed		
Cotton	96	7.4	6.8	5.6	10	86
Cotton linters	94	8.6	7.0	5.7	11	83
Wood pulp	90	8.5	8.3	7.4	9	81
Mercerized cotton	89	13	9.2	7.0	19	70
Viscose rayon	79	26	13.4	9.6	34	45

very little after this time. Under the extreme conditions—*i.e.*, boiling HCl normally used in hydrolysis studies of cellulose accessibility—this change will probably be complete within a few minutes. The hydrolysis-time relationships obtained are thus characteristic of the recrystallized sample instead of the original untreated cellulose. Recent density studies of hydrocellulose have also been shown to support the recrystallization mechanism [5].

Crystallization phenomena of this kind would be expected from theoretical considerations of the method of coagulation of rayons and other celluloses. For example, when crystal nuclei are first formed in a spinning bath, two chains may be caught in two different nuclei with different lengths of each chain between these points of crystallization. With subsequent treatment, these two nuclei cannot merge but will be separated by a region of amorphous cellulose. This amorphous region will be the first attacked by the acid, and as strain induced by crystallization is relieved by chain rupture the loose ends become free to move, and, in the ideal conditions of the hydrolysis medium—*i.e.*, water at 100°C—will allow crystal growth along the chains.

It seems probable, therefore, that crystallization in the early stages of hydrolysis is to a great extent responsible for the low results obtained for cellulose accessibility by these methods. If the moisture regain before and after hydrolysis is taken as a measure of the amount of crystallization occurring, it is possible to estimate the order of magnitude of the error introduced by this crystallization from data given by Nickerson [25]. The data and the estimated corrections are shown in Table VII for samples hydrolyzed in boiling 2.4*N* HCl-0.6*M* ferric chloride for 3 minutes.

The percentage of cellulose crystallized during hydrolysis is estimated by calculation from the moisture regain before and after hydrolysis and equation (1) and by using values of $\sigma_X = 0.17$ and $\sigma_R = 0.28$. The difference in crystallinity calculated in this manner from the moisture regain before and after treatment is taken directly as the increase in crystallinity due to recrystallization (Table VII, column 5). Then, as a first approximation, the corrected crystallinity value is obtained by substracting these values from the original values shown in column 1 of Table VII. This approximation does not take into account any loss in amorphous cellulose during treatment. However, the moisture regains used are those of the original sample and a sample which has been hydrolyzed for only 3 minutes, so that the weight loss involved is very small. Obviously, such a correction cannot be made with great accuracy but it does show a definite trend in that the less crystalline materials crystallize most readily and to the greatest extent. The effect of such a mechanism on determined "crystallinity" or "accessibility" would be to make the whole range of values high and to compress the expected spread of values because of the tendency of the least crystalline celluloses to be most markedly affected. It is interesting to note that the crystallinity values after correction for crystallization occurring during hydrolysis (given in column 6 of Table VII) are of the same order of magnitude as those determined by the physical methods such as deuterium oxide exchange. The crystallization does not seem to affect the relative order of crystallinity values, probably because the degree of ordering which occurs in the aqueous acid is determined by the degree of order present in the original sample, but in certain cases, such as celluloses which have been subjected to dry grinding, the hydrolysis method will fail completely because the ground samples crystallize readily upon wetting. On the basis of the above considerations, it would appear advisable to reconsider published data on the hydrolysis method. Work now in progress in this laboratory seems to indicate that recrystallization phenomena of this type can be clarified by the use of mild hydrolysis as used by Bat-

tista and Coppick [4] in conjunction with the usual high-temperature method.

Nickerson also reported values for the crystalline portion reactivity expressed in arbitrary units as the slope of a hydrolysis-time curve [25]. These reactivities (column 2, Table VII) should be more or less independent of the amount of crystalline material present and will be principally determined by the crystal size and the crystal accessibility. On this basis, the high reactivity of crystalline cellulose from viscose rayon as compared with that from cotton could be accounted for as follows: (1) the crystalline regions in viscose rayon are smaller than those in cotton; (2) the crystalline regions in viscose rayon are more accessible than crystalline regions of the same size in cotton because of differences in crystal form; or (3) the crystalline regions in viscose rayon are both smaller and more accessible than those in cotton. The moisture regains of hydrolyzed cellulose also show this trend. For example, a cotton having an original regain of 6.70 percent and a sample of rayon having an original regain of 13.60 percent have moisture regain values of 5.8 percent and 9.7 percent, respectively, after treatment with 5*N* HCl at 50°C for 5 hours. However, these hydrolysis residues should be almost completely crystalline because of removal of amorphous regions and crystallization accompanying hydrolysis. If this is the case, the observed difference in moisture regain of these celluloses after hydrolysis should be a function only of the difference in size and or accessibility of the crystalline residues, and the higher regain of hydrocellulose from rayon would indicate the presence of small crystalline regions. Although neither of these factors has been thoroughly studied, these measured crystal reactivities and moisture regain values are in qualitative agreement with crystal size and accessibility measurements discussed in this paper, and with the conclusion that crystal size and accessibility are important factors in determining the high reactivity and high moisture sorption capacity of regenerated cellulose.

Summary

The moisture regain of cellulose fibers has been found to be useful as a method of studying the average degree of lateral order or crystallinity of cellulose.

A relative scale of cellulose accessibility determined from moisture regain has been set up on an empirical basis. Possible errors arising from attempts to convert accessibility into percent crystallinity are pointed out. A correction has been postulated to compensate for the differences between the accessibilities to water of native and regenerated cellulose crystals. This postulate leads to the conclusion that accessibility of crystals and or crystal size may be as large a factor in determining different reactivities of different celluloses as are differences in total crystalline content.

Recrystallization has been shown to be a determining factor in acid hydrolysis studies of cellulose at high temperatures, with the result that estimates of crystalline material obtained by such methods are probably high.

The postulates used and the conclusions derived from their use indicate that reconsideration of published data, especially those derived from chemical degradation of cellulose, is advisable.

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Gordon Research Conferences

THE TEXTILES CONFERENCE of the Gordon Research Conferences, sponsored by the American Association for the Advancement of Science, will again be held at Colby Junior College, New London, New Hampshire, the week of July 18.

Requests for attendance at the Conferences, or for any additional information, should be addressed to W. George Parks, Director, Department of Chemistry, Rhode Island State College, Kingston, Rhode Island. From June 15 to September 1, 1949, mail should be addressed to Colby Junior College, New London, New Hampshire.

The program for the 1949 Textiles Conference is as follows:

J. H. Dillon, *Chairman*
Earl E. Berkley, *Vice-Chairman*

July 18—H. Mark—"Principles for the Selection of Fiber-Forming Materials"
R. C. Houtz—"'Orlon' Acrylic Fiber: Chemistry and Properties"

July 19—Milton Harris—"The Nature of the Felting Phenomenon and of Some Anti-Felt Treatments"
E. L. Skau—"A Calorimetric Investigation of the Cellulose-Water Relationships in Textile Fibers"

July 20—William Utermohlen—"Detergency Studies"
T. E. Morton—"Dyeing of Cellulose Considered as a Diffusion Process"

July 21—J. W. Rowen—"Some Infrared Studies on Cellulosic Compounds"
Joseph Brant—"Discussion of Crease-Resistant Treatments of Fine Cotton Fabrics"

July 22—Robert Hoffman—"Relationship of Fiber Properties to Fabric Properties"

Small-Angle X-Ray Scattering in Various Cellulose Fibers and Its Relation to the Micellar Structure*

A. N. J. Heyn†

Abstract

The study of the molecular structure of cellulose fibers by x-rays has been concerned until very recently with diffraction of only relatively wide angles. Almost no work has been done on the diffraction and scattering of x-rays within very small angles adjacent to the primary beam. The only fact known was that such "small-angle scattering" is produced by ramie and viscose rayon.

In the present study, the small-angle scattering by various cellulose fibers has been investigated and it has been found that the scattering by different fibers is completely different.

The hypothesis that the small-angle scattering in cellulose fibers would be related to the micellar size and distance is substantiated by the fact that an experimental change of those distances results in a corresponding (inverse) change in the extent of the scattering. On this basis the difference in the scattering patterns of different fibers is explained as a difference in the size and distance of the cellulose micelles or crystallites.

An orientation of crystallites is also expressed in the small-angle diffraction pattern giving rise to the interesting phenomenon of "cross" formation when the crystallites form an angle with the long axis of the fiber. The angle between the intersecting lines of the cross proved to be related to the pitch of the spiral of the crystallites in the fiber.

Introduction

Study of the structure of matter by use of x-rays has, until very recently, been concerned principally with diffraction at relatively wide angles, with little attention having been paid to the diffraction and scattering at small (or low) angles. In the latter case diffraction and scattering are determined within very small angles adjacent to the central undeviated (primary) beam. As diffraction angle and spacing vary inversely, such studies furnish information on the presence of large spacings in the material investigated. Since this modification of x-ray research is still in the first stage of development, a complete interpretation of all phenomena observed cannot yet be given.

It will be shown in this paper that in cellulose fibers the method described will furnish information on the micellar structures, whereas the conventional method reveals the molecular structure within the micelles. The term "micelle" as used in this paper is equivalent to "crystallite" or "crystalline area" in the light of modern theories.

The distance, size, and orientation of micelles in a fiber are of greatest importance to the explanation of its properties and only a few methods exist at present for the study of the micellar structure, such as double-refraction and electron-microscope techniques.

For this reason the use of small-angle x-ray scattering can be expected to open new possibilities in the study of textile fibers. The experimental results reported in this paper may be considered as only an initial step in the study of the micellar structure of fibers by the use of small-angle x-ray scattering.

Corey and Wyckoff [10] and Fankuchen and Mark [13] have pointed out the possible value of small-angle studies in general. The former have clearly distinguished between two types of scattering and illustrated these with various examples. In one case the small-angle diffraction is discontinuous and consists of several separate, long-spacing diffraction lines or spots which could be related with the presence of a "superidentity" period inside the large molecules present. The technique and interpretation are basically the same as those used customarily in x-ray investigations and are only an extension of the technique at smaller angles. The structural units revealed are parts of large molecules.

This first type of small-angle scattering has been employed mainly in the field of fibrous proteins and

* This paper was read at the meeting of the Fiber Society, Boston, Massachusetts, September, 1948.

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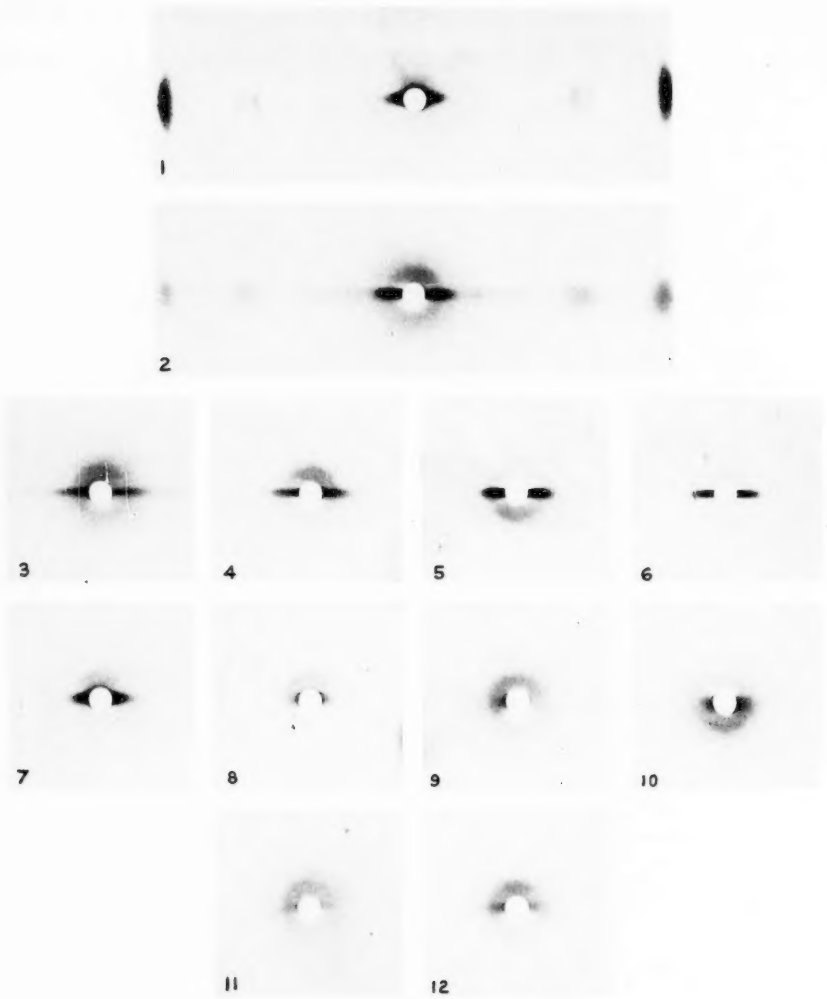

PLATE I. *Small-angle x-ray scattering of different cellulose fibers.*

(1) Equatorial small-angle interference and wide-angle scattering of ramie. (2) The same as (1), for jute. (3) Small-angle scattering of American hemp (Cannabis). *(4) Retted flax. (5) Jute. (6) Roselle* (Hibiscus sabdariffa). *(7) Ramie. (8) Cotton. (9) Cotton. (10) Mercerized cotton yarn. (11) Viscose (Narco). (12) Viscose (Super-Narco).*

TABLE I. SCATTERING AND APPROXIMATE IDENTITY PERIODS FOR DIFFERENT FIBERS

	Hemp	Flax	Jute	Ramie	Viscose	Merc. cotton	Cotton
Maximum scattering angle	2°	1°42′	1°35′	1°18	1°9′	51′	36′
Smallest period (in Å.)	22	26	27	34	38	51.5	73
Average period (in Å.) as calculated from midpoint scattering	44	51.5	55	68	73	95	146

viruses, and data have been obtained which indicate the existence of superspacings inside the molecules from 25 to 725 Å.*

The other type of small-angle diffraction is continuous, with no separate diffraction lines being present. The term "scattering" may be more appropriate here and will be used hereafter in this article. This type of scattering has been studied mainly in nonfibrous material such as carbon black and similar substances, and has been related with the size of small particles present.†

Only a few sporadic data exist on small-angle diffraction by cellulose fibers. It has been known for some time that the ramie fiber gives a continuous scattering. Herzog, Mark, and Hengstenberg, cited by Mark [26], and Kratky and Schoszberger [21] gave a description of the scattering by this fiber, and Kratky [20] ventured a quantitative evaluation which will be discussed below. The only other cellulose fiber for which small-angle scattering has been described is viscose. Corey and Wyckoff [10] published a diffraction pattern of this material and mentioned the absence of sharp reflections "in the band of unresolved scattering," stating that "the meaning of this band is not yet clear." Clark and Parker [9] published small-angle patterns on ramie and rayon. Kratky, Sekora, and Treer [22] and Kratky and Wurster [23] used a special viscose product (prepared after Hermans [17]) in their fundamental research directed toward an interpretation of the phenomena of scattering.

A comparative study of small-angle scattering by various textile fibers has been undertaken by the author, and the results of a study of cellulose fibers will be given here.‡

I: Experimental Data on the Angle of Scattering in Various Cellulose Fibers

For a comparative study of different fibers a special method was worked out, by which the same amount of material was always exposed to the x-ray beam under identical circumstances as far as possible. For this purpose the following method was applied. In a slit a bundle of accurately paralleled fibers 4 cm. in length and 10 mg. in weight was mounted and exposed to an x-ray beam which passed through it at a right angle. Alignment of beam, distance from film, exposure time, and conditions of developing the film were always the same. A fine pinhole beam of 0.025-inch diameter was used, the primary beam being carefully intercepted by a lead disc of 4-mm. diameter. Under these conditions the low-angle pattern of most of the bast fibers proved to consist of two lines on the equator on both sides of the primary beam. (Compare Plate I.)

The length and the width of these lines were different in different fibers, as can be seen in Plate I; the maximum angle of scattering for each is given in Table I. The angle of scattering diminished in following order: hemp, flax, jute, roselle, and ramie. Also the width and intensity were different, jute having a wide and intense scattering, flax a much finer, narrower line, and ramie an almost triangular scattering area, tapering toward the end. The rayons, as far as investigated, have shown a rather diffuse scattering line of short length. In higher oriented rayons like Super-Narco the line became more sharply defined as compared with the less oriented Narco. The cottons had an extremely short line which hardly appeared from underneath the intercepting disc. It is remarkable that in mercerized cotton yarn the line is longer than in cotton.

II: Interpretation of Data, Based on Experiments on Swelling and Mercerization

An attempt will now be made to give an interpretation of the continuous small-angle scattering described above. A survey of existing literature re-

* *e.g.*, Bernal and Crowfoot [6], Wyckoff and Corey [30], Astbury and Sisson [2], Corey and Wyckoff [10], Bernal and Fankuchen [7], Bear [4], Fankuchen [13], MacArthur [25].

† Debye [11], Krishnamurti [24], Warren [29], Biscoe and Warren [8], Guinier [15], and Hosemann [19].

‡ A preliminary note appeared in *J. Am. Chem. Soc.* **70**, 3138 (1948).

veals that a general agreement between various investigators has not yet been reached.

The evaluation of continuous small-angle x-ray scattering has been based by most authors—*e.g.*, Debye [11] and Guinier [15] (*cf.* second footnote on page 165)—on principles similar to those applied to the explanation of the scattering of ordinary light by small particles (Fresnel and Fraunhofer). This interpretation has been principally applied to the x-ray scattering by disperse systems, where the distances between the particles are relatively large as compared with their size and where the distribution in space is random. A comparison has been made with the molecules in a gas, where the intensities scattered by the individual particles are summed to give the total scattering—no phase relationship exists between the particles. This type of scattering is found in the nonfibrous material previously mentioned.

Kratky [20] maintained that for systems designated as densely packed, a completely different interpretation and evaluation of scattering is necessary. In such systems the spaces between the particles are small, as compared with the size of the particles themselves. When such systems are irradiated, a phase relationship between the individual particles may be expected, a fact which to a large degree determines the resulting scattering. This type of system would be generally found in high polymers in the solid state, and most fibers probably belong to it. Due to the dense packing, the particles are arranged with some degree of regularity, which results in the phase relationship mentioned.

Kratky ventured an evaluation of this scattering by the ramie fiber, assuming that the principle of Bragg's law may be applied here for calculating the average identity period (distance of the particles). He assumed that the diffuse scattering originates from an irregular lattice, of a varying identity period. In order to find the average period, the radiation energy belonging to the subsequent values of the identity periods was calculated by dividing the corresponding intensities by the squares of the identity periods. In ramie a maximum intensity of scattering was found at an identity period of 50–60 Å. This period was considered as the average repeat period, and the hypothesis was made that it was indicative of the size and distance of the micelles present. This hypothesis was supported by earlier data of Hengstenberg and Mark [16], who found the same value for the size of the micelles of this fiber (without intermicellar distance) as determined from the width of interference lines in the ordinary x-ray diagram. This agreement in dimensions would indeed strongly substantiate Kratky's hypothesis had Hosemann [19] not arrived at quite different results. Hosemann found the most frequent periodicity in the same material to be 7 Å. when evaluating the data according to the principles applied by Guinier and others (see above). This discrepancy resulted in a controversy between Hosemann and Kratky wherein Kratky rightly pointed out the difference between the two systems described. His argument, however, that his method of evaluation was preferable because it gave a better value for the size of the micelles cannot be considered as convincing, since his assumption that the periodicity was related to the micelles was the very hypothesis to be proved. A better approach was made by Kratky, Sekora, and Treer [22] and Kratky and Wurster [23], who showed that on imbibition of a viscose preparation with various organic liquids the intensity of the scattering varies, and is proportionally related to the differences in the electron densities of the cellulose and the liquid taken up.

From the above it may be clear that the interpretation of the phenomenon of continuous scattering is not yet substantiated, although Kratky's hypothesis and evaluation seem probably correct. In order to bring more direct proof to the hypothesis, the author has approached the problem from another angle: If Bragg's law (and not the principles of Debye, Guinier, and others) may indeed be applied for calculating the structural periodicities, and if these periodicities are identical with the micellar distances, it would follow that a proportional relationship must exist between the extent of the scattering zone and the size and distance of the micelles. Under such conditions a change in this distance in the same material would show itself immediately by a change in the extent of the scattering area (an increase in the micellar distances resulting in a decrease of the length of the scattering line and vice versa). A method for experimentally altering this distance can be found in the application of swelling. It is well known that swelling of cellulose consists in an uptake of liquid only in the spaces between the micelles (intermicellar swelling (Katz)*).

This would result in an increase of the distances between the micelles and therefore also of the distances between the centers of the micelles. Experi-

* This follows from the fact that the wide-angle x-ray diffraction pattern before and after moistening of the fiber is the same.

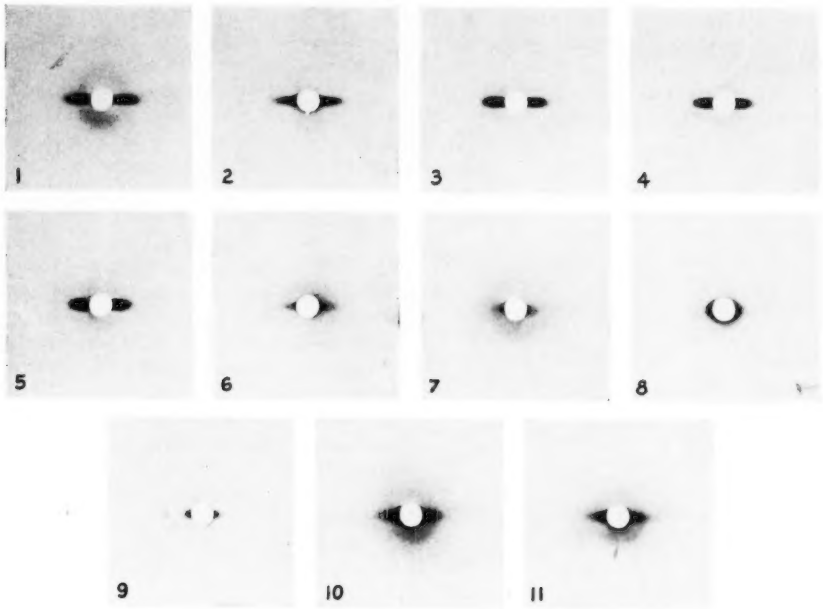

PLATE II. *Influence of the deposition of gold and of swelling on the small-angle scattering in jute.*

(1) Untreated. (2) After deposition of gold in the intermicellar spaces. (3) In water. (4) In 0.5% sodium hydroxide. (5) Same after washing. (6) In 5% sodium hydroxide. (7) In 18% sodium hydroxide. (8) Same after drying. (9) Same after washing and subsequent drying. (10) Ramie, untreated. (11) Ramie mercerized under tension.

ments to ascertain the effect of swelling upon scattering might therefore be expected to provide direct proof of a relation between the micellar distances and the size of the scattering area and afford a crucial test of Kratky's hypothesis. This proof would be of direct importance for the interpretation of the experimental data described in section I.

The results obtained in the following experiments are in complete accord with what might be expected on the basis of the above assumptions. Micellar distances and length of the scattering area proved to vary inversely.

The experiments were carried out by exposing the same sample of 10 mg. of the fiber to the x-ray beam before and after wetting with water or with various concentrations of sodium hydroxide. The moisture content of the fiber was maintained either by continuous addition of the fluid to the freely mounted fiber or by insertion of the fiber, after removing excess liquid, into a closed capillary, in which case the dry fiber compared was also enclosed in the same capillary. The jute fiber was selected for most of the experiments, as it has the clearest, longest scattering line. Experiments with flax were also carried out but did not give different results.*

Results on Swelling in Water

From microscopic study it has been observed that the jute fiber swells some 20% in water. From the images obtained (Plate II, figures 1 and 3) it can be seen that a slight decrease in length of the scattering line resulted on swelling in water. It is remarkable that the line became more intense and had greater width than before. The phenomenon was reversible upon drying. Absorption of radiation by the added water cannot explain the phenomenon or interference since the intensity was not decreased. Moreover,

* This was important, as it is known that in jute lignin is also present and may interfere with the x-ray diagram (Sen and Woods [27] and Banerjee, Basak, and Sen [3]).

shortening the exposure time to a half or a third of the normal one did not result in any decrease in the length of the scattering line. In the following experiments comparisons of the fiber in various swelling solutions were made with reference to the fiber in water.

Results on Swelling in Solutions of Sodium Hydroxide, and on Mercerization

Jute fiber was studied in solutions of 0.5%, 5%, and 18% sodium hydroxide (Plate II). Before and after each treatment (all treatments were carried out with the same fiber) the fiber was washed in water and studied in this fluid. At the concentration of 0.5% the scattering area was almost the same as in pure water, and the process was still reversible. In the 5% solution the scattering area was smaller. Treatment with 18% sodium hydroxide resulted in a much smaller area as compared with the lower concentrations; removal of the alkali upon washing did not result in a restoration of the original scattering; a permanent change had occurred. This is in agreement with the fact that at higher concentrations of alkali mercerization takes place, which treatment results, with most fibers, in a permanent increase in volume and a change in other properties. It is known that the molecules are rearranged into another lattice; very little information is available, however, as to whether the original size of the micelles is retained after this treatment. The permanent decrease of the scattering area observed is in agreement with a permanent increase in the distances of the micelles. When the fiber treated with 18% alkali is not thoroughly washed before drying, a slightly different pattern is obtained which shows scattered intensities also in other directions than the equatorial. This might suggest a smaller degree of orientation and a greater irregularity in the distribution of the micelles.

The results obtained after mercerization of cotton and ramie with 18% sodium hydroxide were different. The mercerization was carried out with and without tension. As has been stated, the lines of scattering in the case of untreated cotton are so short that they hardly appear from underneath the intercepting disc. Upon mercerization under tension, the scattering lines became much longer (compare figures 8, 9, and 10, Plate I); without tension, this effect does not occur. The increase of the scattering line observed in mercerization of cotton under tension is also irreversible, and can only be explained—as far as present data are concerned—by a lengthwise breaking down of micelles, resulting in a distance between micelles of half the original distance, and a proportional displacement of diffracted radiation in the direction of larger angles. During the rotation of micelles into the new lattice and the swelling of the fiber such splitting might be conceivable, especially in connection with the spiral structure and twisted shape of cotton.* The observed higher scattering of mercerized cotton was also observed in commercial mercerized yarns (figure 10, Plate I) and may be a promising method for studying the colloidal background of the process of mercerization.

In ramie, mercerization had little effect upon scattering (see figures 10 and 11, Plate II), although indication of a shortening of the triangular area at its end was present. This may be considered to be in accordance with the presence of large micelles and small intermicellar distances in this fiber (compare section III).

Results on "Dry Swelling" by Deposition of Gold in the Fiber

Another means tried for forcing the micelles apart —without introducing a solution so that the dry material could be compared—was the deposition of gold in the fiber. The well-known method of Ambronn [1] and Frey-Wyssling [14] was followed, in which the fibers are immersed in a gold chloride solution and subsequently exposed to ultraviolet light.

The presence of metallic gold in the fiber could be proved by the x-ray pattern, which showed the well-known superposition of the pattern of cellulose and of gold.

The small-angle diffraction pattern of jute and other fibers treated with a 5% solution of gold chloride always showed a definite decrease in intensity of the scattering, especially at the ends of the lines, and a decrease in width (Plate II, figures 1 and 2). This can be explained by assuming that the gold fills only part of the intermicellar crevices, the others remaining intact or at least not changing their size to such an extent as to affect the scattering.

Conclusion

From the above experiments the assumption of a relationship between the extent of the scattering area

* According to modern ideas the formation of convolutions in cotton might be connected with the crystallization process upon drying and therefore reswelling and untwisting upon mercerization might inversely interfere with the micellar structure.

and the micellar structure appears to be permissible since any experimental change in the distances between the micelles resulted in a corresponding (inverse) change in the extent of the scattering area. Therefore, an evaluation of the data is given below along the lines suggested by Kratky—namely, by the application of Bragg's law.

III: A Calculation of Micellar Distances in the Various Fibers Investigated

The scattering has a great intensity near the primary beam and over some distance away from it; it rapidly decreases near the end of the scattering zone.

The smallest identity period in each fiber can be readily calculated from the greatest angle of scattering. The calculation of the average identity period is more complicated; the distribution of intensities over the subsequent identity periods might be calculated according to Kratky's method, described previously. An exact calculation of our data, however, will be postponed until later, as it is hoped that a quicker and more reliable determination of intensities may be worked out. For a rough approximation and for comparative purposes it will be sufficient to calculate the average identity period from the midpoint of the scattering area. The results obtained in this way are given in Table I.

The values in Table I calculated by application of Bragg's law refer to any repeat period of the micellar and intermicellar structure. As the repeat period of this system can be related only with the alternation of crystalline (micellar) and amorphous (intermicellar) matter, the values may be considered to represent the center-to-center distance between the micelles or, what is the same, the center-to-center distance between the intermicellar spaces.

In many instances the diameter of the micelles will be closely related with the intermicellar distances, especially in natural fibers where the amount of amorphous portion is generally a small part of the total amount of cellulose. In this case the values of the distances will be nearly equivalent to the diameter of the micelles. Moreover, it is possible accurately to determine the ratio between amorphous and crystalline cellulose by other means (*e.g.*, chemically) and hence to calculate exactly the diameter of the micelles from their distances.

In rayons the situation differs from that in the natural fibers, since ratio of amorphous to crystalline cellulose is much higher. In agreement herewith the small-angle scattering indicates large distances between the (small) micelles by a short scattering line of less pronounced character and intense diffuse scattering, presumably due to the large amount of irregularly distributed material.

It may be of interest in this connection to mention that the method used for the evaluation of the scattering by diffuse systems permits a direct determination of the size of the particles (compare Introduction).

At any rate the center-to-center distances of the micelles and their orientation may be considered to be of greater importance than their size, as these distances are directly connected with the texture of the fiber (micellar skeleton) and hence with its mechanical and other properties.

In connection with these and other considerations the data obtained, therefore, can be explained by the presence of smaller intermicellar distances and probably smaller micelles in hemp, flax, and jute; larger micelles and smaller distances between the micelles in ramie and cotton; and, presumably, smaller micelles and larger intermicellar distances in viscose (the latter in connection with the diffuse scattering).

The results may be generalized by stating that a variation exists in the micellar distances in different fibers, and, more precisely, that the frequency curve of the distribution of micellar distance and size has different mean values and different minimum values (and probably also different maximum values) in the different fibers.

These results are of interest in connection with several aspects of current theories on micellar structure —*e.g.*, the question of the existence of the individual micelle, the mechanism of crystallite formation from dispersed cellulose, structural changes accompanying the drying of cellulose, and other phenomena. Also a comparison with results obtained by others in studies of disintegrated cellulose, by the electron microscope, is of particular interest. A discussion of these problems would be beyond the scope of the present article, however.

The explanation of differences of intensities in scattering of different fibers—*e.g.*, jute—is not yet clear; higher intensity may possibly be related to a higher degree of structural regularity. In jute the presence of lignin (compare footnote, page 167) might also play a part. The decrease of intensity on deposition of gold would be in accordance with the first explanation, since a greater irregularity would result from the forcing apart of the micelles in that way.

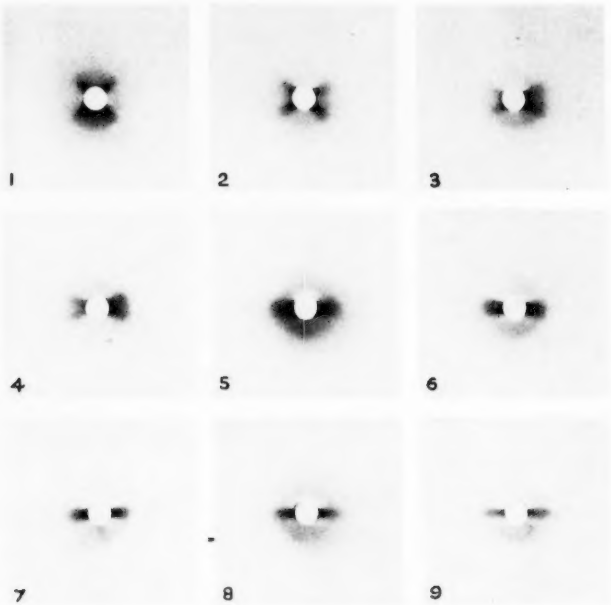

PLATE III. *Small-angle x-ray scatterings of different "hard" fibers.*

(*1*) Cocos nucifera (*coir*). (*2*) Agave lophantha (*Tula ixtle*). (*3*) Agave heteracantha (*Ixtle de Jaumave*). (*4*) Agave fourcroydes (*Mexican henequen*). (*5*) Sansevieria guineensis (*African bowstring*). (*6*) Agave sisalana. (*7*) *Yucca*. (*8*) Musa textilis (*Manila hemp*). (*9*) Ananas comosus.

IV: The Relation Between Scattering and Micellar Orientation

The results described above were obtained with bast fibers and some other fibers having almost parallel orientation of the cellulose micelles to the fiber axis. Employing a fine pinhole beam resulted in a scattering pattern consisting of a horizontal line on the equator on both sides of the primary beam, the line having the same width over its total length (except in ramie).

In addition, studies were made of fibers in which the micelles form angles with the long axis of the fiber; the so-called hard fibers are a good example. The following fibers were studied (Plate III): *Cocos nucifera* (coir), *Borassus flabellifera* (Palmyra), *Agave lophantha* (Tula ixtle), *Agave heteracantha* (Ixtle de Jaumave), *Agave fourcroydes* (Mexican henequen), *Agave sisalana* (Sisal hemp), *Sansevieria guineensis* (African bowstring), *Yucca sp.*, *Ananas comosus* (Pineapple), *Musa textilis* (Abaca, or Manila hemp). In all these cases the small-angle image consisted of two lines intersecting at the center of the diagram (primary beam), forming a "cross" at an angle, presumably identical with the double angle between the axis of the micelles and the fiber axis. In Sansevieria, for instance, the angle was about 20°; in Agave, 45°; and in Cocos (coir, in which the fibrils (micelles) make an angle of 45° with the long axis) the two scattering lines intersect at exactly 90°. It will be noted (Figures 5–9) that in the case of small angles the scattering lines, which have a definite width, will more and more overlap, thus approaching a single line the width of which decreases as the angle becomes smaller. The other angles of the fibers investigated can be easily measured from their low-angle patterns.

A comparison of the characteristics of the small-angle scattering of these fibers with the corresponding wide-angle diagram is very interesting.

It is a well-established fact (Polanyi) that the wide-angle diagram in cases such as the above consists of arcs the size of which increases with increasing angles between the crystallites and fiber axis.

A method for direct determination of the angle of orientation of the crystallites from the size of the arcs has been developed by Sisson [28], and this method has been applied for the practical study of cotton by Berkley [5].

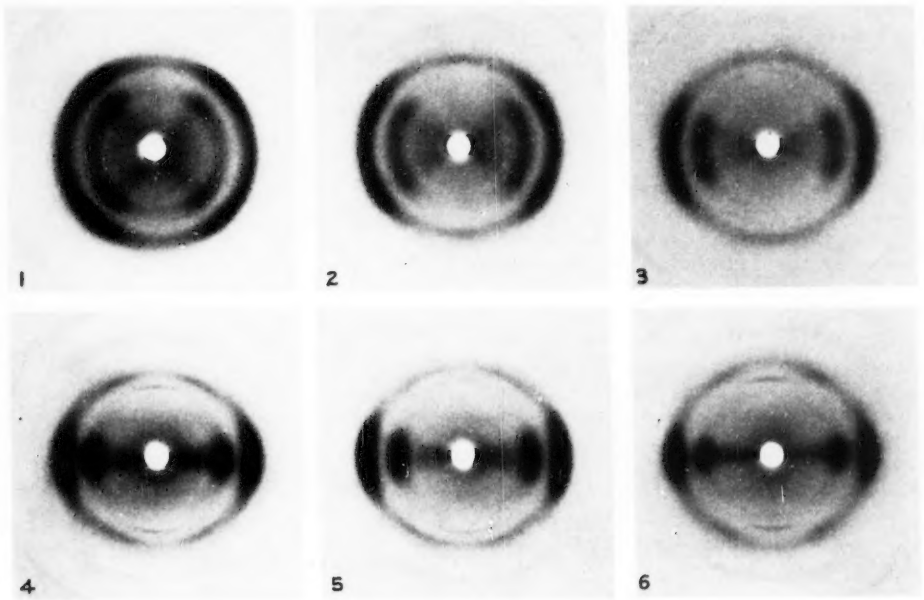

PLATE IV. *Wide-angle diffraction diagrams.*

(*1*) Cocos nucifera. (*2*) Agave lophantha. (*3*) Agave fourcroydes (*Mexican henequen*). (*4*) Sansevieria guineensis (*African bowstring*). (*5*) Agave sisalana (*Sisal hemp*). (*6*) Musa textilis (*Manila hemp*).

The exact determination of crystallite orientation from the arcs is not very simple, since, apart from the spiral pitch of the crystallites, other factors, such as variation of crystallites around random orientation, are involved. The end point of the arcs is very indistinct as its intensity gradually decreases towards the end. The above-mentioned authors suggested the measurement of the 002 arc at a point where the intensity is a definite percentage of the intensity at the equator. A more accurate but much more complicated method has been recently worked out by J. J. Hermans, P. H. Hermans, Vermaas, and Weidinger [18].

Plate IV shows the wide-angle diagrams of some of the fibers investigated. The diagrams have been arranged in the order of decreasing angles of crystallites with fiber axis, as indicated by decreasing size of the 002 interference arc. A comparison of the diagrams of the fibers in Plate IV with the small-angle diagrams in Plate III reveals that here the fibers can be arranged in exactly the same order with reference to the size of the angle between the intersecting scattering lines. Therefore it may be concluded that different spiral pitch of the crystallites goes hand in hand with differences in the size of the angles between the scattering lines.

This result is in agreement with our previous conclusion that the scattering line originates from diffraction by the micelles and that it is perpendicular to their direction. If this is true, the angle between the intersecting scattering lines will be twice the angle between crystallites and fiber axis.

A point of difference between the wide-angle diagrams and the small-angle diagrams consists in the fact that the wide-angle diagram always shows a continuous 002 arc of increasing angular size in the various fibers, whereas the small-angle diagram does not show continuity between the two intersecting scattering lines of the "cross," although the size of the angle between those lines goes hand in hand with the size of the wide-angle arcs. The small-angle image evidently represents only the angle formed by opposite parts of the micellar spiral at the two points where the radius is parallel to the x-ray beam, and

the micelles at the side of the spiral obviously do not play a great part in the small-angle scattering. Since these micelles are parallel to the fiber axis, as seen from the direction of the x-ray beam, their scattering would result in a line on the equator which is actually absent. The same micelles, however, produce wide-angle interferences on the equator, originating from their planes parallel to the long axis.*

From the standpoint of practical application, the small-angle diagram might be important, therefore, as it would allow a direct measurement of the orientation of the crystallites.

The phenomenon of "cross" formation is also important as indicating that (total) reflection or refraction of x-rays on the surface of the fibers does not play an important role in causing the scattering. Such reflection would only cause a scattering perpendicular to the surface of the fibers, as actually is observed in the cases where the crystallites are parallel to the fiber axis. The formation of crosslike scattering where the crystallites form an angle with the fiber axis rules out this possibility, however, indicating that the scattering depends on the internal structures. Otherwise, equatorial scattering would result also in the latter case, the orientation of the surface being the same in both cases.

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* An explanation of this difference in the case of the wide-angle diagram might be possible on the basis of a theory of lamellar micelles.

(*Manuscript received September 12, 1948.*)

Book Reviews

The Chemical Technology of Dyeing and Printing. Louis Diserens. Translated and revised from the Second German Edition by Paul Wengraf and Herman P. Baumann. New York, Reinhold Publishing Corp., 1948. 500 pages. Price, $11.00.

(Reviewed by George H. Schuler, E. I. du Pont de Nemours & Company)

Dr. Diserens' book enjoyed wide popularity in the technical field in Europe and the generally good English translation makes it available to a wide circle of interested technicians in this country. Additions by the translators serve to increase its value to American readers, and the deletions will not be missed. All fields of dyeing and printing have not been covered—for example, direct, diazotized, and developed acid and basic dyes and their methods are barely mentioned, but their characteristics and dyeing properties have been adequately handled in many available texts.

The treatment of the ordinary vat, soluble vat, insoluble azo, and mordant dyes is thorough and complete, with respect to both dyeing and printing. There is, possibly, more emphasis on printing; and the dyeing of vat colors, for example, might have been given more detailed attention, considering the growing importance of this group of dyes in that field. However, a great deal of attention has been paid to auxiliary products used as assistants in dyeing and printing, and the book undoubtedly will appeal to many because of this feature.

Bibliography and patent references are well handled, having been incorporated largely in the text, and are usually given in some detail. In fact, one wonders whether the greatest value of this book will not be that it furnishes so many references for further study. Although the many details quoted from patents testify to the thorough literature survey which preceded its publication, the patents are not classified by the author as to their significance and industrial importance.

The American edition has, for the most part, maintained the typographical standard of its European original and is easy to read. An error or two have been perpetuated from the German edition and some unimportant errors have been introduced in the translation.

While this book will not serve as a complete text on the chemical technology of dyeing and printing, its thorough treatment of the subjects presented greatly extends the borders of those subjects, compared with previously available texts. It should be a desirable addition to technical libraries and prove of worth to individuals interested in this branch of science.

Genius of Industrial Research. D. H. Killeffer. New York, Reinhold Publishing Corp., 1948. 257 pp. Price, $4.50.

(Reviewed by Joseph H. Brant, Bates Manufacturing Company)

The informality and straightforwardness of the preface are retained throughout this book. The preface exemplifies these qualities when it states that "The material presented comes predominantly from the field of industrial chemistry, for in no other is research so important, so well developed, and so fruitful. For this, no apology is offered physicists, biologists, sociologists, psychologists, and others interested in research.—So too, others of diverse backgrounds and interests may be led to understand and appreciate research methods—possibly even to use them—by reading here the fascinating accounts of how many important modern developments were achieved."

Throughout, the book has the aspect of a "*Reader's Digest*" presentation, since the separate chapters have been devoted to different aspects of exemplifying the title and the objective. Each chapter contains well-chosen quotations to supplement the author's own observations and opinions concerning the immediate subject. For this reason, the reviewer found it easy to lay the book aside, but correspondingly easy to resume its perusal without too serious a loss of continuity or interest. As is to be expected of a presentation of this kind, some divergence of opinion exists from chapter to chapter which may be considered healthy rather than stifling, since useful ideas need not necessarily be ones which meet with general agreement.

The fifteen chapters present a logical sequence, beginning with Chapter 1, "Industrial Research Is Methodical," and proceeding through a course of consideration to Chapter 13, "Evaluating Research," Chapter 14, "Something about Patents," and, finally, Chapter 15, "Loose Ends Gathered Here." A determined effort has been made to provide the interested reader with a series of references, from which parts of the book have been drawn, and a study of which would, no doubt, serve to broaden one's view.

Each chapter is introduced by one or more quotations which seem very apropos. Facetiously, the reviewer caught himself asking the question whether the chapter was written to fit the quotation, or whether other quotations to be found in the literature might apply just as aptly to the meditations of other readers.

Chapter 15 provides this quotation: "So, from a great diversity of problems must come the equally great diversity of solutions, and the available variety of methods of attack must be equal to these demands. That, of course, leads inevitably to the conclusion that the prime objective of this book, to set forth the pattern of industrial research, is quite impossible to attain." Even though one might be forced to agree with this opinion in the ultimate analysis, nevertheless a significant accomplishment has been achieved.

It is impossible to pick out the points of greatest interest, but the reviewer perhaps enjoyed Chapter 9, "The Progressive Development of an Idea," as much as any other. On the other hand, Chapter 12, "Reports are Essential," contained many interesting and useful suggestions.

Few errors occur in the book and the type is clear, making reading more pleasant. The reviewer anticipates returning to it from time to time for inspiration as well as for useful information and well-chosen quotations.

Studies on the Elasticity of Cellulose Fibers. Volume I. R. W. Asmussen and Frode Andersen. *Transactions of the Danish Academy of Technical Sciences*, No. 5, 1947. Address: Dansk Textilforsknings Institut, Polyteknisk Laereanstalt, 83 Solvgade, Copenhagen K, Denmark.

(Reviewed by Milton M. Platt, Fabric Research Laboratories, Inc.)

In Volume I of this series, apparatus is described for determining the visco-elastic characteristics of single cotton fibers. The following mechanical properties have been determined at various humidities: stress relaxation at various constant deformations; stress-strain diagrams at slow rates of extension; the dynamic stiffness (the product of dynamic modulus and cross-sectional area) versus amount of stretch and or tension determined at frequencies of 15–30 cycles/second; and the internal friction. The results indicate that tensional stiffness decreases with increasing humidity for both the static and the dynamic loadings, with the static properties more greatly influenced by humidity than the dynamic. Dynamic stiffness at constant humidity increases both with the magnitude of the tension (or stretch) and the frequency, but is much less influenced by the latter than by the former. It is shown that for the various mechanical properties investigated, differentiation must be made between relative humidity of 100% and the liquid state. For example, dynamic stiffness and static tensile strength are less, while maximum elongation is greater at the liquid state. At all humidities the stress-strain diagrams of cotton fibers are essentially linear.

Studies on the Elasticity of Cellulose Fibers. Volume II. Frode Andersen. *Transactions of the Danish Academy of Technical Sciences*, No. 6, 1947. Address: Dansk Textilforsknings Institut, Polyteknisk Laereanstalt, 83 Solvgade, Copenhagen K, Denmark, 1947.

(Reviewed by Milton M. Platt, Fabric Research Laboratories, Inc.)

The methods described in Volume I were utilized to study differences between staple rayon fibers and cotton fibers. The following comparisons were observed: While cotton fibers possess essentially linear stress-strain diagrams at all humidities, the rayon fiber diagrams range from concave down at 0% R.H. to concave up at liquid water. At 37% R.H.–70% R.H. the typical rayon diagram containing a yield point at about 30–50% of the ultimate load is obtained. At any humidity, considering the great variances which exist, the initial static stiffness (measured at very light loads) of cotton and staple rayon fibers is the same. The dependency of the dynamic stiffness of the rayon fibers upon both tension and humidity is about the same as that for cotton. Relaxation tests on the staple rayon indicate

the viscous component to be non-Newtonic, the data being best explained by assigning a number of gradually increasing values of the relaxation time.

High-Polymer Physics. Edited by Howard A. Robinson. Brooklyn, New York, Chemical Publishing Company, Inc., 1948. 572 pages. Price, $12.00.

(Reviewed by Lee P. Witnauer, Eastern Regional Research Laboratory)

The purpose of this book is to bring together in one volume American contributions to high-polymer physics in the last few years. The book contains 23 papers, each by authors outstanding in the field. These are not, in general, review articles, but are reprints of original papers which have already appeared, at least in part, in scientific journals.

The book is divided into four parts. The first part, entitled "Determination of Molecular Structure of High Polymers," contains 3 papers on the structural studies of glass, synthetic rubber, and polygalacturonides.

Part II, "The Physical Properties of High Polymers," contains the majority of the 23 articles. Mechanical, elastic, viscometric, dielectric, stress-strain, thermal, and electrostatic properties are considered, as well as crystallization and tackiness. Among the polymers investigated are rubber and synthetic rubber, cork, textiles, and plastics.

Part III, "The Chemical Physics of High Polymers," contains 5 papers which deal with molecular distribution, viscosity, thermal polymerization, swelling, and the thermodynamic characteristics of certain high polymers.

Three papers are included in the last part, entitled "Instrumentation and High Polymers." One paper describes the use of thermal diffusion columns in the study of polymer solutions. The other two describe instruments for making light-scattering measurements.

The subject-and-author index is very complete. It is unfortunate that some of the bibliographies are so limited.

The collection of papers included in this volume provides a valuable source of information on the current picture of high-polymer physics, for both the physicist and the chemist.

Correction

"Mechanics of Elastic Performance of Textile Materials: II: The Application of Sonic Techniques to the Investigation of the Effects of Visco-Elastic Behavior upon Stress-Strain Relationships in Certain High Polymers," December, 1948, issue, page 705:

On page 712, second column, last paragraph, third line: η should appear as the left-hand term of the equation.

On page 715, Figure 9: "STRENGTH" should be "STRETCH."

ABSTRACTS

SERVICES AVAILABLE

Reprints of the original articles abstracted in TEXTILE RESEARCH JOURNAL *are often available from the publishers. Otherwise, it may be possible to obtain copies of the periodicals. Orders should be sent direct to the publishers.*

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The JOURNAL *is again offering to its subscribers reprints of the Abstracts and Book Reviews sections, printed on one side of the sheet so that the items may be clipped, pasted on cards, and filed for permanent reference. Subscriptions to this service for 1949 are $3.50 each. Orders for this special service should be mailed at once to Textile Research Institute, Inc., 10 East 40th Street, New York 16, N. Y.*

A list of periodicals, the abbreviations used in reference to articles, and the addresses of publishers of English-language publications is given in the January, 1949, issue, page 46.

ANALYSIS: TESTING: LABORATORY METHODS

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End Groups of Amylose and Amylopectin

Starch. I. End group determination of amylose and amylopectin by periodate oxidation. A. L. Potter and W. Z. Hassid. *J. Am. Chem. Soc.* **70**, 3488-90 (Oct. 1948).

A method for estimating the end groups of amylose and amylopectin is described. This procedure is based on the quantitative determination of the formic acid produced when the starch fractions are subjected to oxidation with sodium meta-periodate at 2°C. The amylopectins from 6 different plants ranged from 22 to 27 glucose residues per end group. The chain lengths of the corresponding amyloses ranged from 420 to 980 glucose residues. Authors

Text. Research J. Mar. 1949

Molecular Weights of Amyloses and Amylopectins

Starch. II. Molecular weights of amyloses and amylopectins from starches of various plant origins. A. L. Potter and W. Z. Hassid. *J. Am. Chem. Soc.* **70**, 3774-7 (Nov. 1948).

The number-average molecular weights of 6 amylose and 5 amylopectin components of starches from different plant sources were determined by osmotic pressure measurements. Those of the amyloses range from 100,000 to 210,000; those of the amylopectins, from approximately 1,000,000 to 6,000,000. Comparison of the molecular weights determined by osmotic pressure measurements with those estimated from the chain-length values found by the periodate end-group method indicates that in some amyloses (potato and Easter lily) single molecules constitute single chains. In other amyloses (tapioca, wheat, corn, and sago) 2 or 3 chains may be linked to form one amylose molecule. In the case of amylopectins the number of side chains is approximately 1,000. Authors

Text. Research J. Mar. 1949

Breaking Strength

The value of breaking-strength tests as quality control in dyeing and finishing. A. Schaeffer. *Textil-Praxis* **3**, 311-13 (Oct. 1948).

The author considers breaking strength of the yarns of finished and/or dyed fabrics to be a poor criterion for quality control. He recommends single-fiber tests and determination of the degree of polymerization instead. J. F. Krasny

Text. Research J. Mar. 1949

Color-Fastness

Determination of color-fastness. J. Weibel. *Textil-Rundschau* **3**, 309-12 (Sept. 1948).

A brief history of the various attempts and methods to determine color-fastness. The Swiss textile industry is adopting methods used in the U. S. and Great Britain rather than the German methods which were previously used. J. F. Krasny

Text. Research J. Mar. 1949

Fiber Sorters

Fiber sorters aid cotton mill operation. S. Carter. *Textile World* **98**, 109, 192, 194, 196, 198 (Dec. 1948).

The fiber sorter may be used in the mill to determine the fiber length (through fiber length distribution arrays), to determine the spinning qualities of new lots of stock, and to arrange bale mixes, check the per-

formance of the card and comber, and establish nep counts.

A. L. Landau

Text. Research J. Mar. 1949

Formaldehyde Resin Finishes

Identification of formaldehyde resin finishes on cellulose fibers and wool. R. Aenishänslin. *Ciba Rundschau* **1948**, 2953 (through *Textil-Praxis* **3**, 365 (Nov. 1948)).

1 g. of fibrous material is extracted twice with 50 cm.^{3} of alcohol for 3 min. per extraction at boiling temperature and rinsed three times with 50 cm.^{3} of distilled water. The fibers are treated with 50 cm.^{3} of 1% hydrochloric acid and about 3 cm.^{3} of distillate are obtained. 2 cm.^{3} of the distillate are treated with 5 mg. carbazol in 5 cm.^{3} of sulfuric acid. In the presence of formaldehyde, a blue or blue-green color appears. 5 cm.^{3} of the acid extract are treated with 1 cm.^{3} of a 5% ammonium molybdate solution; albumin or melamine resins yield a white turbidity. If this test is positive, 5 cm.^{3} of acid extract are treated with 1 cm.^{3} of a 1% picric acid solution. Melamine resins cause strong turbidity or precipitation; albumin causes turbidity only when present in large amounts. If the test result is doubtful, 1 cm.^{3} of 5% potassium ferrocyanide is added to 5 cm.^{3} of the acid extract. Melamine causes turbidity; albumin and urea resins do not. 10 cm.^{3} of acid extract are treated with 1 cm.^{3} of concentrated hydrochloric acid and 0.1 cm.^{3} of 0.1*N* sodium nitrite solution. At intervals of 5 min., spot tests are made on iodine potassium starch paper. If the initial HNO_2 reaction disappears in 30 min., urea is very likely present. If this test is positive, 5 cm.^{3} of the acid extract are mixed with 31 cm.^{3} of a 10% copper sulfate solution. If thiourea is present a pale green turbidity or precipitate appears.

Text. Research J. Mar. 1949

Potato Starch Gels

Potato-starch gels. H. T. Whittenberger and G. C. Nutting. *Ind. Eng. Chem.* **40**, 1407–13 (Aug. 1948).

In an 8% concentration pasted at 90°C potato starch forms gels which are not as firm as those from corn or wheat but firmer than tapioca, waxy corn, or waxy sorghum, which form gels too soft to test. Data are given on strength, firmness, and clarity, and on the effect of pH, temperature, and concentration. Gel strength, measured by the Delaware Jelly Tester, increased linearly with concentration between 6% and 11%. A pH below 4 or above 9.5 weakened the gels. Preheating at 93°C with 28% water retarded swelling, increased firmness and strength, and lessened clarity and tackiness. The addition of hydrogen bonding agents, such as sucrose, dextrose, or glycerol, increased the fluidity of the hot pastes, lessened clarity and tackiness, but increased gel firmness and strength. High concentrations inhibited granule swelling. Using oblique illumination, the granule condition of various pastes are shown in photomicrographs. The extent of granule swelling and persistence of granule sacs are correlated with gel strength.

A. R. Macormac

Text. Research J. Mar. 1949

Hand-Knitted Yarns

Evaluation of hand-knitted yarns by technological tests. O. Heimeran. *Textil-Praxis* **3**, 335–9 (Nov. 1948).

Bulkiness (related to thermal conductivity), elasticity, and resistance to abrasion are important qualities of hand-knitted yarns. Bulkiness can be measured by winding the yarn around a glass plate, covering it with another plate upon which a known pressure is exerted, and measuring the distance between the 2 plates. This value and the value found by measuring the width of a predetermined number of yarn layers are used in formulas for the calculation of "porosity," which is defined as the percentage of air in a yarn (based on total volume). A good yarn should contain about 85% of air by volume. Load-elongation properties are investigated with the Frenzel-Hahn apparatus. In this device moving yarn is subjected to a predetermined constant load; the number of breaks per unit length is recorded, and load-elongation diagrams are drawn continuously. Results are given for various wool, rayon staple, and mixed yarns.

J. F. Krasny

Text. Research J. Mar. 1949

CHEMICAL and PHYSICAL RESEARCH

★

Oxidation of Cellulose

Atmospheric oxidation of cellulose in ammoniacal copper solution. V. I. Ivanov and E. D. Stakheeva-Kaverzneva. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* **1945**, 492–503; cf. *C. A.* **40**, 3894^8 (through *Chem. Abstr.* **42**, 6109*i* (Aug. 20, 1948)).

The lowering of the η of cuproammoniacal cellulose solutions on keeping is due to reaction with atmospheric oxygen, resulting in oxidation of the CH_2OH group in the glucose residues to CHO and CO_2H. This, in turn, lowers the resistance of the glucoside links to bases. The velocity of the reaction increases rapidly with temperature increases and, in addition to depolarization, H_2O-soluble degradation products of low molecular weights are produced. These amount to 8% after 200 hrs. at 10–15°C, and to 25% after 5 hrs. at 30°C, and contain 1% of HCO_2H, AcOH, and CO_2, and approximately 30% of uronic acids. The reaction mechanism is discussed.

Text. Research J. Mar. 1949

Viscosity of Cellulose

The influence of pitch in wood cellulose on its viscosity. L. A. Kantor and P. B. Kheifetz. *Bumazh. Prom.* **22**, No. 4, 32–4 (1947) (through *Chem. Abstr.* **42**, 6112*e* (Aug. 20, 1948)).

Experimental results are presented to show that cuprammonium viscosity of bleached and unbleached wood cellulose is dependent not only on the degree of depolymerization and the number of cellulose bonds

but, to a great degree, on the presence of pitch in the cellulose, a pitch content greater than 1% increasing the indicated viscosity several-fold, with no change in mechanical strength.

Text. Research J. Mar. 1949

Flow in Cellulose Fibers

Relaxation and flow in cellulose fibres. R. Meredith. *J. Text. Inst.* **39**, P245–52 (July 1948).

Eyring's theory of rate processes applied to flow in textile fibers is outlined. The theory is applied in explaining the shape of the creep curves for viscose rayon, acetate rayon, and cotton. The energy of activation of a cotton yarn is calculated from stress-strain curves at different rates of loading. A similar value is obtained from stress-relaxation experiments on the same yarn. L. P. Witnauer

Text. Research J. Mar. 1949

Primary Hydroxyls in Cellulose Acetate

The determination of primary hydroxyl groups in cellulose acetate by tosylation and iodination. Carl J. Malm, Leo J. Tanghe, and Barbara C. Laird. *J. Am. Chem. Soc.* **70**, 2740–7 (Aug. 1948).

Eight samples of cellulose acetate containing from 32.3–41.4% acetyl were tosylated with *p*-toluene sultonal chloride in pyridine and then iodinated by sodium iodide in acetonylacetone. The longer the time of tosylation, the greater the amount of iodine introduced. The primary alcohol groups can be estimated by noting the point at which the iodination reaction slows down. In some cases, the amount of iodine introduced exceeded the tosyl groups present, owing to the presence of chlorine groups in the tosyl compound. As the reaction conditions in both the tosylation and iodination were extended, increasing amounts of primary hydroxyl were indicated. Therefore, in order to use this reaction as a means of determining primary hydroxyls, the reaction conditions must be standardized. Authors

Text. Research J. Mar. 1949

Fabric Geometry

The relationship between the structural geometry of a textile fabric and its physical properties. I. Literature review. S. Backer. TEXTILE RESEARCH JOURNAL **18**, 650–8 (Nov. 1948).

This is the first in a series of papers to be issued by the Quartermaster Corps discussing the importance of fabric geometry in the development of more utilitarian and serviceable textile materials. It is a literature review which shows the relationship between the structural characteristics of fabrics and various functional characteristics, such as breaking strength and elongation, tear-resistance, thermal-insulation, abrasion-resistance, and gas permeability. Author

Text. Research J. Mar. 1949

Flax Quality

The relationship between the chemical composition and the quality of flax fiber. M. Ludtke. *Melliand Textilber.* **28**, 37–40 (1947); cf. *C.A.* **42**, 5678*d* (through *Chem. Abstr.* **42**, 6541*d* (Sept. 10, 1948)).

The experimental results of previous papers are summarized and discussed. It is concluded that certain rules are apparent when a large number of samples are considered, but no regular relationship between the chemical and physical properties of flax fiber has been discovered.

Text. Research J. Mar. 1949

Gelation

The effect of concentration and temperature on gelation time. Gopal S. Hattiangdi. *J. Colloid Sci.* **3**, 207–11 (June 1948).

An empirical equation of the form $t = ac^{-Q/RT}$ has been presented which represents the variation of the setting time (t) of a gel with both concentration (c) and temperature (T). This functions as a modified type of Arrhenius' equation at constant concentration, and expresses the kinetics of gelation at constant temperature. Plots of log t vs. $(\log c)/T$ yield a straight line, suggesting that reaction order varies with temperature, and activation energy, with concentration. The condition of equal setting time, achieved with increasing concentrations at elevated temperatures, is possibly the point of balance between (1) the concentration of primary colloidal particles and (2) the extent of secondary aggregation, the latter being dominant at low concentrations and temperatures, and the former at higher ones.

Text. Research J. Mar. 1949 Author

Tensile Properties of Jute

Some tensile properties of jute. R. R. Mukherjee, M. K. Sen, and H. J. Woods. *J. Text. Inst.* **39**, P241–4 (July 1948).

Young's modulus and tensile strength measurements for single jute fibers are reported. Young's modulus is found to be correlated with fineness. The effect of specimen length on the tensile strength is qualitatively in accordance with the "weak link" theory. The results indicate that good-quality jute is comparable in strength with other blast fibers. L. P. Witnauer

Text. Research J. Mar. 1949

Karayu and Locust Bean Gum

Physicochemical properties of Karayu gum and locust bean mucilage. J. V. Kubal and N. Gralén. *J. Colloid Sci.* **3**, 457–71 (Oct. 1948).

The following data were obtained: sedimentation and diffusion constants at zero concentration, molecular weight from these and from partial specific volume, frictional ratio and average length and width of the molecule. Karayu gum has a molecular weight of about 30 times that of locust bean mucilage despite the fact that intrinsic viscosities of the two are the same. The differences are due to molecular shape and solvation. E. D. Klug

Text. Research J. Mar. 1949

Lignin Structure

Constitution of the side chains of lignin. A. V. Wacek and K.

Kratzel. *J. Polymer Sci.* **3**, 539–48 (Aug. 1948).

Conclusions are drawn regarding the probable structure of the side chain of lignin based on a comparison of the behavior of lignin with that of model compounds in (1) sulfite reactions, (2) alkaline oxidation reactions with nitrobenzene, and (3) hot alkali reactions. No new data. E. D. Klug

Text. Research J. Mar. 1949

Molecular Weight Distribution

Distribution of molecular weights of pectin propionates. Harry S. Owens, Jackson C. Miers, and W. Dayton Maclay. *J. Colloid Sci.* **3**, 277–91 (Aug. 1948).

A sample of pectin propionate was fractionated by fractional precipitation. Intrinsic viscosity of the fractions is directly proportional to the number-average molecular weights. The molecular weight distribution curves are Gaussian and do not have Kramer and Lansing's logarithmic shape. E. D. Klug

Text. Research J. Mar. 1949

Polymeric Esters

Polymeric phosphonitrilic esters. A new type of inorganic-organic plastic. F. Goldschmidt and B. Dishon. *J. Polymer Sci.* **3**, 481–6 (Aug. 1948).

Polymeric phosphonitrilic chloride was treated with aliphatic alcohols (ethyl, isoamyl, and 2-ethylhexyl) in pyridine at room temperature. Most of the chlorine was replaced by alkoxyl but some was also replaced by oxygen. The resulting esters, insoluble but swollen in organic solvents, were solubilized by adding a swelling agent during alcoholysis or by refluxing in tetrachloroethane. Physical properties of the products and data on the properties of a butyl ester-nitrocellulose composition are given.

Text. Research J. Mar. 1949 E. D. Klug

Polysaccharide Carbamates

Polysaccharide aryl carbamates. Ivan A. Wolff and Carl E. Rist. *J. Am. Chem. Soc.* **70**, 2779–82 (Aug. 1948).

By treating the carbohydrates in dry pyridine with phenyl isocyanate or alpha-naphthyl isocyanate, the tricarbanilates or tri-alpha-naphthyl carbamates have been prepared. The melting characteristics, solubility behavior, and optical rotation of the tricarbanilates of corn starch, corn amylose, and amylopectin, potato amylose and amylopectin, waxy corn starch, glycogen, beta-amylase limit dextrin, corn torrefaction dextrin and Shardinger beta-dextrin and of the tri-alpha-naphthyl-carbamates of corn strach, amylose, and amylopectin are reported. A fully esterified ester of the untreated starches was obtained. The tricarbanilates of branched and unbranched polysaccharides can be differentiated by their wide variation in specific rotation and their different solubility in ethyl acetate.

Text. Research J. Mar. 1949 Authors

Refractive Index of Proteins

The specific refractive increment of some purified proteins. Gertrude E. Perlmann and L. G. Longsworth. *J. Am. Chem. Soc.* **70**, 2719–24 (Aug. 1948).

With the aid of a hollow, prismatic cell and the optical equipment of the Tiselius electrophoresis apparatus, the refractive index increments of solutions of egg albumin, bovine serum albumin, human serum albumin, beta-lacto-globulin, and human gamma-globulin have been measured as functions of the protein concentration, the temperature, and the wave length of the incident light. The changes in the specific refractive increment that occur on titration of the protein with alkali in the presence of neutral salts, and after equilibration, with buffers, have also been determined. Such data are necessary for a quantitative interpretation of the electrophoretic patterns of proteins. Authors

Text. Research J. Mar. 1949

Surface Tension

Mixed monolayers. I. Adsorbed films at the air-water surface. Eric Hutchinson. *J. Colloid Sci.* **3**, 413–23 (Oct. 1948).

The surface tension of a solution containing octyl alcohol and sodium dodecyl sulfate was measured and the concentrations of alcohol and detergent were calculated. The alcohol is the main constituent in the film even when it is present in low concentrations. The properties of the mixed film indicate no interaction between the components.

Text. Research J. Mar. 1949 E. D. Klug

Titration of Viscose

Potentiometric titration of viscose. P. Herrent and G. Jnoff. *J. Polymer Sci.* **3**, 487–99 (Aug. 1948).

The pH changes occurring during titration of viscose solutions were not sharp enough to enable determination of the degree of ripening of viscose. However, potentiometric titration with $AgNO_3$ using silver and calomel electrodes gave curves with points of inflection which varied with the degree of ripening. A plot of the e.m.f. at the point of inflection vs. degree of ripening gives a minimum at the optimum degree of ripening for spinning. The titration curves indicate that sodium dithiocarbonate is formed during ripening. The scheme of the reactions occurring during ripening is postulated.

Text. Research J. Mar. 1949 E. D. Klug

BLEACHING: DYEING: FINISHING

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Bleaching Cellulose

Cellulose. Bleaching with sodium chlorite. A. Klein. *Teintex* **11**, 285, 287, 289–91, 293, 321–5, 327, 349–51, 353–4 (1946); *J. Text. Inst.* **38**, A163 (1947) (through *Chem. Abstr.* **42**, 6112*b* (Aug. 20, 1948)).

A systematic study has been carried out of the bleaching action of $NaClO_2$ and of its behavior towards cellulose. The results obtained are compared with those obtained from

the use of other bleaching agents, such as H_2O_2 and NaClO. The problem of the effect of the presence of metals on the stability of the bleach has also been studied. The "length" of the bath was 1:10 in the case of staple fiber and 1:6 for cotton. Whiteness degrees were determined before and after ageing, and break-resistance, degree of polymerization, and degradation coefficient were also determined. The pH was ascertained throughout the operation. Experiments with staple fiber and with cotton are fully described and all results are presented in graphs and tables. It is shown that $NaClO_2$ bleaching can lead to a higher degree of whiteness than the H_2O_2 treatment if the operation is carried out at a pH below 4. In practice this will necessitate a modification of existing equipment in order to prevent corrosion and spontaneous decomposition of the chlorite by catalysis. For continuous chlorite bleaching, provision must be made for the continuous addition of a more concentrated solution to compensate for losses due to decomposition, and a permanent pH control is necessary, as the chlorite solutions have the tendency to reach a pH between 5 and 6.

Text. Research J. Mar. 1949

Bleaching of Jute

Bleaching of jute with chlorite. P. B. Sarkar and H. Chatterjee. *J. Text. Inst.* **39**, T274–81 (Aug. 1948).

The color of jute fibers is ascribed to the presence of fats, waxes, chlorophyll, and lignin. The article deals primarily with the removal of lignin by means of sodium chlorite. Under proper conditions the lignin can be removed to any degree desired, complete removal resulting in a full white color. 11 tables of data present the effect upon the jute of the bleaching agent under various conditions of time, concentration, temperature, pH, and yarn/liquor ratio. Jute is more sensitive to chlorite than is cotton or flax. Scouring prior to bleaching had a very detrimental effect upon its strength. The lignin may be completely removed and yet the jute will retain its fibrous structure and a considerable portion of its strength, in contradiction to some previous observations. However, it is admitted: "For reasonable wet strength . . . and a fair degree of whiteness . . . no suitable conditions could be found with chlorite for bleaching jute. For a pale yellow color . . . 0.5% chlorite at 1:10 yarn/liquor ratio and 65–70°C seems to be suitable." 16 references. J. Tallant

Text. Research J. Mar. 1949

Cross-Dyeing Cotton-Rayon Fabrics

Cross-dyeing cotton-rayon fabrics. Anon. *Am. Wool and Cotton Reptr.* **53**, 17–18 (Sept. 16, 1948).

Cross-dyeing of a fabric is possible only if the two fibers used are of different compositions. Matching of shades is difficult if the fibers are of different basic luster or have a variation in twist. A. L. Landau

Text. Research J. Mar. 1949

Pigment Resin Emulsions

Pigmented resin emulsions for printing and pad dyeing. M. Silverman. *Am. Dyestuff Reptr.* **37**, P44–6 (Jan. 26, 1948).

The constituents of pigment resin emulsions and the mechanics of making them are discussed. K. S. Campbell

Text. Research J. Mar. 1949

Vat Acid Dyeing

Practical experience in vat acid dyeing. J. H. Hennessy. *Am. Dyestuff Reptr.* **36**, P775–7, P784 (Dec. 29, 1947).

Practical examples are described in which the finer particle size of vat acid leuco preparations and their more rapid conversion into the sodium leuco form are utilized to advantage: these include dyeing pale shades on singles cotton yarn and spun rayon in package form, spun rayon fabrics, fabrics containing protein fibers, and fabric constructions containing nubs. K. S. Campbell

Text. Research J. Mar. 1949

Screen Printing

Silk screen printing of pigments in color. J. W. Nee. *Ind. Finishing* **24**, No. 9, 56–8, 60, 62, 64, 66 (1948) (through *Chem. Abstr.* **42**, 7049*a* (Sept. 20, 1948)).

Requirements of process lacquers for decorating pennants subject to outdoor flying, the screen printing and drying on a production basis, and what long exposure and performance tests revealed about color, fungus attack, etc., are noted.

Text. Research J. Mar. 1949

Mothproofing

Chemical and physiological aspects of moth protection. H. Luttringhaus. *Am. Dyestuff Reptr.* **37**, P57–62 (Jan. 26, 1948).

The chemical nature of some of the most effective moth-proofing agents is discussed; agents included are DDT, Mitin, and the Eulans. The physiology of the clothes moth and the eating habits of the larva are described. Photomicrographs are presented. K. S. Campbell

Text. Research J. Mar. 1949

Trends in Fabric Processing

Trends in fabric processing. F. Tripp. *Textile Bulletin* **74**, 71, 72, 74 (Dec. 1948).

A discussion of the processes involved in finishing, particular the improvements that have been made which have decreased the time required for complete finishing. A. L. Landau

Text. Research J. Mar. 1949

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

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Drying and Shading Printed Cotton Fabrics

Drying and shading printed cotton fabrics. Anon. *Am. Wool and Cotton Reptr.* **53**, 9–10, 67 (Nov. 18, 1948).

The operation and maintenance of the machinery used for the drying and shading of printed cotton fabrics. The comparative advan-

tages of different methods are discussed. A. L. Landau
Text. Research J. Mar. 1949

Fabric Shrinkage

Shrinkage of woven cotton and staple-fiber fabrics. E. Franck. *Tids. Textilteknik* **6**, 91–6 (1948) (through *Chem. Abstr.* **42**, 7049g (Sept. 20, 1948)).

The causes of shrinkage and ways of reducing it mechanically (special machines) and chemically (synthetic resin, alkali, and formaldehyde treatments) are reviewed.
Text. Research J. Mar. 1949

Preshrinking Knitted Fabrics

The Redman process for controlling shrinkage of knitted fabrics. A. W. Williams. *Textile Age* **12**, 42, 46, 48, 50 (Oct. 1948).

A discussion of the technical features of the Redman process for preshrinking knitted fabrics. Suggestions are given for testing cotton tubular knit fabric for shrinkage in laundering. A. L. Landau
Text. Research J. Mar. 1949

Bibliography on Industrial Fibers

Chemical engineering materials of construction—Fibers. R. S. Casey and C. S. Grove, Jr. *Ind. Eng. Chem.* **40**, 1793–8 (Oct. 1948).

An annotated bibliography arranged alphabetically by authors of articles (1944–1948) containing information of value to engineers interested in the use of fibers in industry. The physical and chemical properties of fibers and their engineering and industrial applications, but not methods of testing or manufacturing, are covered. A. R. Macormac
Text. Research J. Mar. 1949

Regenerated Protein Fibers

Regenerated protein fibers from wool and casein. R. L. Wormell. *J. Text. Inst.* **39**, T219–24 (July 1948).

Regenerated protein fibers are prepared from a degradation product of wool blended with casein by dispersion in 0.5% caustic soda followed by extrusion into an acid and salt bath. The resulting fibers are conditioned in a prehardening bath, stretched, and hardened. Physical properties are reported for the blends and for 100% casein. The tenacities of the blends are lower and the ratios of wet tenacities to dry tenacities are greater than for 100% casein. L. P. Witnauer
Text. Research J. Mar. 1949

Modernization of Wool Carding Machines

Accent on production. Anon. *Platts Bull.* **6**, 83–90 (Sept.–Oct. 1948).

A review of the means by which wool carding machinery can be modernized. L. A. Fiori
Text. Research J. Mar. 1949

Axminster Looms

Axminster carpet looms. Anon. *Platts Bull.* **6**, 96–7 (Sept.–Oct. 1948).

An improved knife motion employed on wide looms connected with the method of pile severance known as "top cutting" is described.
Text. Research J. Mar. 1949 L. A. Fiori

Electric Controls on Looms

Electric controls on modern looms. Anon. *Textile Recorder* **66**, 61–2 (Sept. 1948).

Electrical devices controlling main operating loom motions which are featured on Swiss rayon and silk automatic looms are described and illustrated diagrammatically.
Text. Research J. Mar. 1949 L. A. Fiori

Slashers and Slashing

Slashers and slashing. A. E. Silcox. *Textile Age* **12**, 44, 46–48, 50–51 (Nov. 1948).

The proper procedure to be followed in starting up a slasher is outlined. Formulas and calculations necessary for estimating the production of the slasher, and tables showing drying rates and production for various models of slashers are given.
A. L. Landau
Text. Research J. Mar. 1949

Slashers and slashing. A. E. Silcox. *Textile Age* **12**, 58, 60, 62–4, 66 (Dec. 1948).

The preparation of size mixtures is detailed with particular reference to the amount of agitation and temperature recommended at various stages of cooking and storing. Size kettles, cooking and storage, and size pumps are described and their proper use is explained.
A. L. Landau
Text. Research J. Mar. 1949

Bunching Motion for the Mule

Pirn bunching motion for automatics. Anon. *Platts Bull.* **6**, 94–5 (Sept.–Oct. 1948).

Illustrated and described briefly is a motion for the woolen mule which enables the machine to spin packages that can be used in the loom, without necessitating a further process of re-winding where the "bunch" is normally formed. The device is automatic and can be disengaged when spinning warp yarns.
Text. Research J. Mar. 1949 L. A. Fiori

Ring Frames—Conversion

Conversion, ring frames. Anon. *Platts Bull.* **6**, 68–70 (July–Aug. 1948).

In a previous report (*Platts Bull.* **6**, 40–8 (May–June 1948); cf. *T.R.J.* **18**, 703 (1948)) ring spinning frame drafting conversions covered only the 4-roller high-drafting system. In this discussion the alteration of existing frames to the single-apron system of high-drafting is described in detail. L. A. Fiori
Text. Research J. Mar. 1949

Saco-Lowell Worsted System

New Saco-Lowell system for processing worsted yarn. J. L. Beacon. *Textile Age* **12**, 34, 39, 42 (Nov. 1948).

The new Saco-Lowell system for spinning worsted yarn is discussed with regard to its effect upon both the cotton and worsted industries. The system is limited at the present time to the use of fibers having a staple length of $3\frac{3}{4}$ in. or under.

Conditioning and marking of the top before processing is explained.
A. L. Landau
Text. Research J. Mar. 1949

Saco-Lowell system for processing worsted. J. L. Beacon. *Textile Age* **12**, 42, 46, 48–9 (Dec. 1948).

The new Saco-Lowell system for spinning worsted consists of a lap winder, two processes of drawing, roving, spinning, winding, and twisting. On the lap winder there are two sets of drafting rolls having only a small tension draft. The drawing frames are equipped with a new drafting system composed of 3 lines of top rolls over 4 bottom rolls. The drawing frames are equipped with baller motions, instead of the conventional coilers, to be used in conjunction with cans.
A. L. Landau
Text. Research J. Mar. 1949

Yarn Knotter

Semi-automatic knot tying. Anon. *Textile Weekly* **42**, 862 (Oct. 15, 1948).

A knotter suitable to tie yarns which may vary widely in count, turns per inch, quality, and material. Claim is made that it will tie any knot on any textile. L. A. Fiori
Text. Research J. Mar. 1949

MISCELLANEOUS

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Mohair Production and Use

Mohair report. Livestock Branch, Production and Marketing Administration, U. S. Dept. of Agriculture, Washington, D. C., June, 1948. 37 pp. Free.

The quality of the mohair clip in the United States has declined, but growers have little incentive to improve it because dealers buy on a flat-price basis. A well-developed promotion program and additional research on grading, marketing, and utilization are needed. Goats are an integral part of agriculture in Texas because they clear brush and prevent crowding-out of forage for cattle and sheep. The use of mohair in automobile upholstery, formerly its most important use, has declined because of consumer objections to its "prickly pile" and warmth, and because cars will sell regardless of upholstery quality. The use of mohair in railroad cars, buses, and planes will continue, but volume is small. The use of mohair in furniture upholstery has declined because of the change in fashion from velvets and plushes to looped-pile and frieze fabrics, and because of the growing use of slip-covers. A large amount is used in lightweight worsteds for suits. Data on production, consumption, imports, and prices are given.
Text. Research J. Mar. 1949 R. B. Evans

Rayon Pulp

Wood. Utilization for rayon and paper. H. Bucher. *Textil-Rundschau* **1**, 16–20 (1946); *J. Text. Inst.* **38**, A372 (1947) (through *Chem. Abstr.* **42**, 6111*c* (Aug. 20, 1948)).

A broad review is given of wood as raw material for the rayon and paper industries.
Text. Research J. Mar. 1949

Rayon Tire Cord

Rayon tire cord fabrics. C. H. Beaver. *Rayon and Synthetic Texts.* **29**, 47 (Oct. 1948).

A brief review of rayon tire cord specifications. L. A. Fiori
Text. Research J. Mar. 1949

Universal Yarn Counts System

A universal yarn counts system. Anon. *Textile Manufacturer* **74**, 454–6 (Oct. 1948).

An outline of the advantages to be realized by the adoption of the proposed universal system for the numbering of all yarns. Conversion factors for various fibers are tabulated. A. L. Landau
Text. Research J. Mar. 1949

Rinsing Water

Automatic control of rinsing water. P. C. Covraux. *Industrie textile* **1948**, 153 (through *Textil-Praxis* **3**, 365 (Nov. 1948)).

The conductivity of the water used in the rinsing of textiles is used as a measurement of its purity. A vertical glass tube containing 2 platinum-covered electrodes is part of a Wheatstone bridge. High frequencies are used to prevent polarization at the electrodes; the potential is about 2 volts.
Text. Research J. Mar. 1949

Tariff on Silk Manufactures

Silk manufactures. Summaries of Tariff Information, Volume 12. U. S. Tariff Commission, Washington, D. C., 1948. 49 pp. Free.

Basic information is presented on imports, tariff status, competition with domestic industries, etc., for each type of silk manufactures imported into the United States.
Text. Research J. Mar. 1949 R. B. Evans

50 Years of Textile Research

50 years of textile research. J. S. Jacobs. *Textile Inds.* **112**, 164, 166, 168, 175 (July 1948).

Credit for the formation of one of the first industrial research laboratories is given to the textile industry, with the establishment by Samuel Luther Dana of a laboratory at the Merrimack Manufacturing Company at Lowell, Mass., in 1834. From studies carried out in this laboratory, the "American system" of bleaching was developed. The general institution of research laboratories by private firms did not commence on a wide scale until after 1900, the Pacific Mills and Cheney Brothers being pioneers in this field and starting slightly before this time. One of the first projects undertaken by the National Bureau of Standards after its establishment in 1901 was the testing of and research on textiles and textile raw materials. The results of important surveys dealing with the development of private research groups are revealed in tabular form and the various trends and comparisons are discussed.
A. L. Landau
Text. Research J. Mar. 1949

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